complete

PROCEEDINGS

OF

THE CHEMICAL SOCIETY.

Vol. XVI. Nos. 217—230.
JANUARY—DECEMBER, 1900.

EDITED BY THE SECRETARIES

LONDON
GURNEY & JACKSON, 1, PATERNOSTER ROW
1901.

RICHARD CLAY AND SONS, LIMITED
LONDON AND BUNGAY

DATES OF ISSUE OF THE MONTHLY NUMBERS OF THE JOURNAL OF THE CHEMICAL SOCIETY TO FELLOWS.

January number was issued		1st January.
February	„	1st February.
March	„	1st March.
April	„	2nd April.
May	„	1st May.
June	„	1st June.
July	„	2nd July.
August	„	1st August.
September	„	1st September.
October	„	1st October.
November	„	1st November.
December	„	1st December.

LIST OF GRANTS MADE FROM THE RESEARCH FUND DURING THE YEAR.

£5 to J. McCrae, for an investigation of some tartaric acid esters of higher alcohols, and the acidyl derivatives of these.

£20 to F. C. Garrett and J. A. Smythe, for an examination of the basic substances contained in the Broxburn shale ore.

£15 to E. J. Russell, for an examination of the effect of the addition of successive increments of moisture on the rate of oxidation of phosphorus.

£15 to A. Lapworth, for an examination of the application of the 'Claisen' reaction to $\alpha\beta$-unsaturated acids and their allied compounds.

£10 to A. Lapworth, to continue the examination of some acids derived from camphor.

£10 to H. O. Jones, to investigate the nature and limits of the isomerism of partially asymmetric nitrogen compounds of the types $NR'R''R'''_2X$ and $NR'_2R''_2X$.

£15 to J. J. Sudborough, to re-determine the esterification constants of some substituted acrylic acids, and to determine them for some *n*-fatty acids, *o*-substituted benzoic acids, and α- and β-substituted propionic acids. To continue work on combination of aromatic bases with trinitrobenzene, &c., and on stilbene derivatives.

£10 to G. D. Lander, to investigate alkylation by means of silver oxide and alkyl halides, more particularly the alkylation of amides and anilides, with production of imino-ethers.

£10 to George Young, to continue investigations into the structure of amidothiodiazoles.

£50 to W. J. Pope, to extend his investigation of optically active substances to compounds of other asymmetric elements than those already described.

£10 to J. Wade, to continue the investigation of the constitution of hydrogen cyanide by ascertaining (a) the mechanism of the conversion of the isocyanides into nitriles, (b) whether the aldehyde compounds with hydrogen cyanide resemble those of isocyanides or nitriles, (c) the cause of the non-formation of isocyanides and the formation of nitriles when potassium cyanide is heated with alkyl iodides in presence of alcohol.

LIST OF FELLOWS ELECTED DURING 1900.

Name.	Proposed.	Elected.
Ashton, James	April 5th	June 21st.
Aston, Bernard Cracroft	November 15th	December 6th.
Bain, Alexander William, B.A.	February 15th	May 3rd.
Baker, Frederick Nolan.	January 18th	February 15th.
Battle, George Edward, B.A.	May 3rd	June 21st.
Bennett, Alexander Hutcheon	December 7th, 1899.	February 15th.
Bennett, George Lowe, M.A.	November 1st	December 16th.
Beringer, Heinrich Rowland	March 15th	May 3rd.
Bilimoria, Hormasji Naoroji, M.A., B.Sc.	November 15th	December 6th.
Binks, Frederick Nisbet	November 1st	,, ,,
Boyes, Herbert James Singleton	,, ,,	,, ,,
Britten, Frank Curzon, B.A.	February 1st	May 3rd.
Brooke, Charles Berjen, jun.	May 17th	June 21st.
Brooke, John Richard	March 15th	May 3rd.
Burnett, Theodore Ridley, Ph.D.	November 1st	December 6th.
Calvert, Sidney, M.A., B.Sc.	December 21st, 1899	February 15th.
Cantin, Angélo	May 17th	June 21st.
Chater, Arthur Brand	March 15th	May 3rd.
Cheeseright, John Henry	November 1st	December 6th.
Cole, Oscar Joseph	December 7th, 1899.	February 15th.
Comber, Albert Walter	November 1st	December 6th.
Cooper, William Francis, B.A.	January 18th	February 15th.
Courtman, Ernest Owen	May 17th	June 21st.
Cullinan, Nicholas, M.D.	March 15th	May 3rd.
Cussons, John, B.Sc.	,, ,,	,, ,,
Davidson, Alexander	November 1st	December 6th.
Davis, Arthur Charles	February 15th	May 3rd.
Davison, Thomas Cuthbert	December 7th, 1899.	February 15th.
Dawson, Harry Medforth, B.Sc., Ph.D.	,, ,, ,,	,, ,,
Deerr, Noël Fielding	February 15th	May 3rd.
Dixon, Stephen M., B.A.	December 7th, 1899.	February 15th.
Donald, William	March 15th	May 3rd.
Eadie, Robert	February 1st	,, ,,
Ellis, Frederic Richard	March 15th	,, ,,
Fechtner, Arthur Louis William	November 1st	December 6th.
Findlay, Alexander, M.A., B.Sc.	January 18th	February 15th.
FitzGibbon, Thomas	March 15th	May 3rd.
Foulds, James	December 7th, 1899.	February 15th.
Fowler, Morris Broad	February 1st	May 3rd.
Freeman, Willie Ludford, B.A.	November 1st	December 6th.
Gasson, William	,, ,,	,, ,,
Gee, Granville Reginald	December 21st, 1899	February 15th.
Geldard, Julius	January 18th	,, ,,
Gibbings, George William	November 1st	December 6th.
Gibson, John	,, ,,	,, ,,
Gompertz, Richard Henry Cyril, B.Sc.	April 5th	June 21st.
Gough, John Henry	May 3rd	,, ,,

Name.	Proposed.	Elected.
Gray, Robert W.	December 7th, 1899..	February 15th.
Gritton, Henry Bertie	May 17th	June 21st.
Halstead, Reginald Gordon	February 1st	May 3rd.
Handcock, Walter Augustus	November 1st	December 6th.
Hargreaves, William Arthur, M.A.	,, ,,	,, ,,
Harker, George, B.Sc.	,, ,,	,, ,,
Hart, Herbert William	November 16th, 1899	February 15th.
Hart-Smith, James	December 7th, 1899..	,, ,,
Harvey, Alfred William	December 21st, 1899	,, ,,
Haynes, James Herbert, B.Sc.	March 15th ..	May 3rd.
Hemingway, Frank C. R.	November 1st	December 6th.
Henderson, John Brownlie	,, ,,	,, ,,
Hewitt, Samuel	,, ,,	,, ,,
Hewitt, William Henry, B.A.	,, ,,	,, ,,
Hinks, Percy John	May 3rd	June 21st.
Houston, Adam	January 18th	February 15th.
Hudson, Edmund Foster, B.A.	June 7th	December 6th.
Hutchin, Henry William	November 16th, 1899	February 15th.
Ichioka, Tajiro	May 3rd	June 21st.
Jackson, Henry Joshua, B.A., B.Sc.	December 7th, 1899..	February 15th.
Jappé, Adolf	November 1st.	December 6th.
Jennings, Henry	March 1st	May 3rd.
Jones, Humphrey Owen, B.A., B.Sc.	November 1st.	December 6th.
Joyce, Thomas Goode, B.Sc.	December 7th, 1899...	February 15th.
Kershaw, James Henry	February 1st	May 3rd.
Kilner, George Washington, M.A.	November 1st	December 6th.
Kynaston, William Charles Robert	December 7th, 1899...	February 15th.
Lamb, Morris Charles	November 1st	December 6th.
Lander, George Druce, B.Sc.	,, ,,	,, ,,
Laws, Arthur Robert	December 7th, 1899..	February 15th.
Leathes, John Beresford, M.A., M.B.	May 17th	June 21st.
Liebmann, Adolf, M.A., Ph.D.	February 15th	May 3rd.
Lockhart, Thomas Lamb	March 15th	,, ,,
Macara, Thomas	February 1st	,, ,,
Mackenzie, Thomas Ebenezer	December 21st, 1899.	February 15th.
Mair, William	,, ,,	,, ,,
McCall, William	November 1st.	December 6th.
McKenzie, Alexander Ernest	April 5th	June 21st.
McNair, Hugh	,, ,,	,, ,,
Menzies, Alan W. Cranbrook, M.A., B.Sc.	December 7th, 1899..	February 15th.
Meyer, Hans, Ph.D.	November 15th	December 6th.
Morgan, John Livingston Rutgers, M.A., Ph.D.	December 21st, 1899..	February 15th.
Morris, Edgar Ford, M.A.	December 7th, 1899...	,, ,,
Morris, Herbert Newall	,, ,,	,, ,,
Munton, Frederick Thomas	February 15th	May 3rd.
Napper, Sidney Scrivener	May 17th	June 21st.
Naylor, Ernest Brooks, B.Sc.	December 7th, 1899..	February 15th.
Nightingale, Thomas Marginson, B.Sc.	November 1st.	December 6th.

Name.	Proposed.	Elected.
Pardy, Alexander	November 1st	December 6th.
Patrick, David Herbert	May 3rd	June 21st.
Paul, John	November 1st	December 6th.
Pearce, Ernest Vivian	,, ,,	,, ,,
Pettigrew, Robert	March 1st	May 3rd.
Phillpotts, Geoffrey Surtees, B.A.	,, ,,	,, ,,
Readman, James Fraser	December 21st, 1899.	February 15th.
Riley, Walter A.	January 18th	,, ,,
Row, M. C. Nanjunda, B.A., M.B.	May 17th	June 21st.
Roy, M. Goolab	,, ,,	,, ,,
Sanders, James McConnell	December 21st, 1899.	February 15th.
Sandford, James Wallace	February 15th	May 3rd.
Sargeant, Fred Pilkington	January 18th	February 15th.
Silberrad, Oswald, Ph.D.	May 17th	June 21st.
Smiddy, Timothy A.	May 3rd	,, ,,
Smith, Edward Shrapnell	January 18th	February 15th.
Smith, Herbert Procter	April 5th	June 21st.
Stapleton, Henry Ernest, B.A.	November 1st	December 6th.
Steele, Bertram D., B.Sc.	February 15th	May 3rd.
Storr, Bertram Vincent, B.Sc.	December 7th, 1899.	February 15th.
Strong, Archie Hugh	,, ,,	,, ,,
Thornton, Arthur Lambert, B.Sc.	November 1st	December 6th.
Tilley, James Walter	February 1st	May 3rd.
Tomlins, George Edward	April 5th	June 21st.
Traquair, John	May 17th	,, ,,
Walker, Augustus John, B.Sc.	February 1st	May 3rd.
Waterhouse, Gustavus Athol, B.Sc.	December 7th, 1899.	February 15th.
Wiechmann, Ferdinand Gerhard, Ph.D.	November 1st	December 6th.
Wilson, Leonard Philip	December 7th, 1899.	February 15th.
Woodbridge, Walter Bourne	November 1st	December 6th.
Wright, Herbert Edwards, M.A.	,, ,,	,, ,,

FELLOWS DECEASED.

Name.	Elected.	Died.
Atkinson, Edmund	March 3rd, 1872	May 4th, 1900.
Borland, John	March 1st, 1877	July 7th, 1900.
Boylan, Alfred Hunter	May 6th, 1897	May 6th, 1900.
Branscombe, William Harcourt	February 16th, 1899	
Conroy, Sir John	January 18th, 1866	December 15th, 1900.
Crawley, Henry Howard	March 16th, 1882	September 12th, 1900.
Edwards, John B.	February 7th, 1848	
Ellis, Thomas Flower	April 17th, 1890	January 24th, 1900.
Harris, Frank W.	February 21st, 1884	August 12th, 1900.
Hotblack, Herbert A.	December 7th, 1882	
Hughes, John Elias	May 4th, 1899	January, 1900.
Lawes, Sir John Bennet	June 17th, 1850	August 31st, 1900.
Manning, Frederick Alfred	February 4th, 1858	December 31st, 1900.
Marcet, William	February 7th, 1853	March 4th, 1900.
McConnell, William	June 18th, 1896	June 24th, 1900.
Parsons, William	May 17th, 1888	April 6th, 1900.
Reynolds, Richard	November 19th, 1857	April 5th, 1900.
Richardson, J. G. F.	December 1st, 1864	January 6th, 1900.
Rylands, Thomas Glazebrook	February 16th, 1870	February 14th, 1900.
Shaw, Saville	February 6th, 1890	November 5th, 1900.
Smith, George	December 20th, 1873	
Thorp, William	February 1st, 1866	February 13th, 1900.
Waage, Peter	January 20th, 1898	January 13th, 1900.
Warden, C. J. H.	December 4th, 1873	July 18th, 1900.
Wood, Augustus A.	December 5th, 1867	September, 1900.
Wyatt, Thomas M.	February 19th, 1891	

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3. On the relationship between the constitution of some substances and the fluorescence which they exhibit. By J. T. Hewitt, M.A., D.Sc.	3	—
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7. Note on the use of a mixture of dry silver oxide and alkyl halides as an alkylating agent. By G. Druce Lander	6	—
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8. The chlorine derivatives of pyridine. Part V. Constitution of citrazinic acid. Formation of αα′-dichloropyridine and of αα′-diiodoisonicotinic acid. By W. J. Sell, M.A., and F. W. Dootson, M.A.	9	233
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12. The absorption spectra of ammonia, &c. By W. N. Hartley, F.R.S., and James J. Dobbie, D.Sc., M.A.	14	318
13. Isoamarine. By Francis R. Japp, F.R.S., and James Moir, M.A., B.Sc.	15	—
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15. The volumetric estimation of potassium. By R. H. Adie, M.A., and T. B. Wood, M.A.	17	1076

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16. On the action of aluminium chloride on camphoric anhydride. III. By F. H. Lees and W. H. Perkin, jun.	18	—
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56. The bromination of benzeneazophenol. By J. T. Hewitt and W. G. Aston	89	712
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ERRATA.

P.	l.	
66	8	*for* "zoeglœa" *read* "zooglœa."
,,	25	,, "hypomicrobium" *read* "hyphomicrobium."
184	6	,, "grams" *read* "grains."
189	1	,, "(5H)" *read* "(8H)."
204	16	,, "$C_{12}H_{19}O_2$" *read* "$C_{13}H_{20}O_2$."
210	37	,, "as represented by" *read* "in accordance with."

RICHARD CLAY AND SONS, LIMITED LONDON AND BUNGAY

Issued 24/1/1900

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 16. No. 217.

January 18th, 1900. Professor Thorpe, F.R.S., President, in the Chair.

Messrs. E. W. Lewis, A. J. Shelton, S. Blofield, and J. N. Goldsmith were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Frederick Nolan Baker, 3rd Royal Iniskilling Fusiliers, Mullingar, Ireland; William Francis Cooper, Ashlyns Hall, Berkhampsted; Alexander Findlay, Emilienstrasse 10[I], Leipzig, Germany; Julius Geldard, 120 Park View Terrace, Otley Road, Bradford; Adam Houston, Brisbane House, Bellahouston, Glasgow; Walter A. Riley, Brunswick Lodge, Newmarket Road, Norwich; Fred Pilkington Sargeant, Springfield Place, Leeds; Edward Shrapnell Smith, 35 Botanic Road, Wavertree Park, Liverpool, E.

Of the following papers, those marked * were read.

*1. "Note on nitrogen halogen compounds." By Julius Stieglitz and E. E. Slosson.

The authors point out that F. D. Chattaway and K. J. P. Orton, in their work on "A Series of Substituted Nitrogen Chlorides, &c." (*Trans.*, 1899, 75, 1046) have overlooked a series of papers emanating from the Kent Chemical Laboratory of the University of Chicago, in which, since 1893, results of work on the nitrogen halogen compounds in

various directions have been given, and a definite line of work undertaken for further investigation. In one of these papers, "Ueber die Einwirkung von unterbromiger und unterchloriger Saeure auf Saeureanilide" (*Ber.*, 1895, **28**, 3265), the preparation and behaviour of acyl-phenyl nitrogen chlorides and bromides are discussed, and some of the compounds obtained by Chattaway and Orton described. In order to avoid future conflict, the line of work pursued by one of the authors and his students is fully outlined as centring in a study of the "Beckmann rearrangement" of acyl-nitrogen halides and analogous bodies.

Further results are given concerning the behaviour of acyl-phenyl nitrogen halides, especially towards alkalis, potassium cyanide, and zinc ethide. All of these reagents reproduce acylanilides. The preparation of acyl-alkyl-nitrogen chlorides and representatives of the series are described: *ethyl benzoyl nitrogen chloride*, $C_2H_5NCl{\cdot}COC_6H_5$, m. p. 53·5°, the corresponding methyl compound is an oil. Alkalis, potassium cyanide, and zinc ethide regenerate the acyl-alkyl-amides.

Further representatives of the isomeric series, the chloro (or bromo) imido-acid esters, $RC(:NCl)OC_2H_5$, &c., are given: *chloroimidoethyl metanitrobenzoate*, $NO_2C_6H_4C(NCl)OC_2H_5$, m. p. 61°, the corresponding *bromide* melts at 71°; the analogous *chloroimide* of *β-naphthoic ethyl ether* melts at 68°, the *bromide* at 77°. These ethers are remarkably stable nitrogen halides, perhaps the most stable known. Some have been distilled without decomposition in a vacuum above 100°; boiling alcoholic ammonia does not decompose chloroimidoethylmetanitrobenzoate. Although a number have been obtained in solid form, no stereoisomeric compounds, $RC(:NCl)OR$, have as yet been observed, such as exist in the case of the analogous benzhydroximic ethers, $C_6H_5C(:NOH)OC_2H_5$. On treatment with zinc ethide, ethylamine derivatives are obtained.

Discussion.

Dr. Chattaway said he regretted that the papers mentioned had been at first overlooked. Dr. Orton and he had approached the subject from an entirely different point of view, and he did not think that their future work was likely to overlap. Professor Stieglitz and his students were working on the Beckmann change, while they were chiefly studying substitution, and endeavouring to show that the chlorination and bromination of anilines and anilides are not direct processes, but that nitrogen chlorides and bromides are always first formed, and under favourable circumstances subsequently undergo isomeric change.

***2. "On the electrolysis of the nitrogen hydrides and of hydroxylamine." By E. C. Szarvasy, Ph.D.**

A short account was given of the experiments of the author on the electrolysis of solutions of ammonia, hydrazine, azoimide, hydroxylamine, and of their salts.

The experiments were carried out at different temperatures, and with varying current densities and concentrations. The conditions were determined under which ammonia, hydrazine, and azoimide, on electrolysis, yield their two components in the proportions contained in their molecules respectively, and without the formation of any secondary products.

In the case of hydroxylamine and its salts, both oxidation and reduction products were formed, no matter how the experimental conditions were varied.

Many attempts were made to prepare polymeric nitrogen by electrolysing solutions of azoimide and its salts at very high current densities; this part of the work is still in hand.

***3. "On the relationship between the constitution of some substances and the fluorescence which they exhibit." By J. T. Hewitt, M.A., D.Sc.**

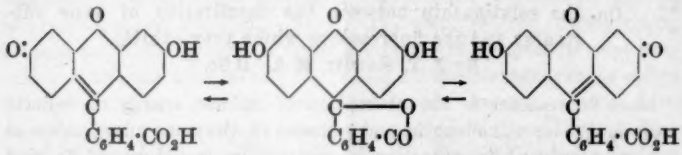
Since fluorescence is the absorption of radiant energy of definite wave-length or wave-lengths and emission of the same energy after it has been reduced in vibration-frequency, one would expect to find fluorescence usually a property of substances capable of existing in tautomeric forms. As a matter of fact, the colouring matters which do exhibit fluorescence are almost without exception tautomeric, the exceptions which are known being usually substances for which no very great degree of purity can be guaranteed.

But many substances which behave tautomerically do not exhibit well-marked fluorescence; this might well be due to the fact that in a solution in which the two tautomeric forms are in equilibrium the reaction-velocities from one form to the other are so small that a very few of the molecules have the opportunity of absorbing energy when they correspond to one and emitting it in the other configuration.

The case is, however, very different when the molecule in one of its configurations is symmetrical; to pass from this to the other configuration, either of two displacements is necessary, equal in magnitude, but opposite in direction. Just as a pendulum (neglecting the friction due to its support and the medium in which it vibrates) swings regularly between two extreme positions, passing at regular

intervals through its lowest point, so a molecule of a substance which exhibits the kind of tautomerism characteristic of fluorescein might undergo continual and frequent change. Fluorescein itself yields derivatives, not only of a phenolic lactone, but also of a quinonecarboxylic acid. The transition from the lactone to the quinonecarboxylic form may be effected by displacement of either of its phenolic hydrogen atoms, the symmetry of the molecule conditioning the equality of energy necessary for displacement of either atom. Hence all the molecules will be undergoing tautomeric change continuously and frequently, and energy absorbed when the molecules have one configuration will be, to an appreciable extent, emitted when they correspond to the other configuration. It is practically certain that the vibration frequency of fluorescein is different in the two states (the diethyl ethers corresponding to the two forms are quite different in the character of their absorption) and hence every opportunity is offered for energy of a rapid vibration frequency to be largely transformed into energy of greater wave-length.

In the case of fluorescein, the condition of a molecule may be symbolised in the following manner:



The greater number of fluorescent dye-stuffs conform to the theory shortly stated above; exceptions may, however, be classed under two heads.

(i) Substances having the requisite structure, but not exhibiting fluorescence.

(ii) Substances exhibiting fluorescence, but not possessing the doubly symmetrical tautomeric structure considered in the case of fluorescein.

It is, however, probable that many of the exceptions are only apparent, the fluorescent spectrum not having been sufficiently examined.

4. "Action of fuming nitric acid on α-dibromocamphor." By Arthur Lapworth and Edgar M. Chapman.

The authors have repeated the work of Kachler and Spitzer on the oxidation of α-dibromocamphor (*Monatsh.*, 1883, **4**, 554), and agree with them that camphoronic acid is produced, but the quantity of this substance is small, and it is difficult to separate it from homocam-

phoronic acid, which is present in much larger amount; on [the other hand, they have not been able to detect any isocamphoronic acid, and conclude that Kachler and Spitzer were merely dealing with impure homocamphoronic acid.

The product, to which Kachler and Spitzer gave the provisional formula $C_{24}H_{33}BrN_4O_{12}$, appears to have been a mixture of the substance $C_{10}H_{16}N_2O_6$, already described by the authors (*Trans.*, 1899, **75**, 986), with ordinary nitrobromocamphor, $C_{10}H_{14}OBrNO_2$, produced by the nitration of monobromocamphor formed in the initial stage of the reaction.

Besides the above-mentioned products and dibromocampholid, a number of other substances seem to be formed. One of these remains dissolved in the water with which the mixture is diluted, and cannot be isolated by dilution. It is obtained by extracting the liquid containing the homocamphoronic acid with chloroform, and forms a neutral oil which is not readily soluble in pure water; it is probably a lactone. When this substance is allowed to remain with aqueous potash, it produces an acid having the formula $C_{10}H_{16}O_4$, which forms magnificent, transparent crystals, is sparingly soluble in water and melts at 177°. When distilled, or warmed with strong acids, it undergoes a curious molecular change, yielding an acid, $C_{10}H_{12}O_2$, melting at 167—168°, which has been identified as trimethylbenzoic acid, (CO_2H : Me : Me : Me :: 1 : 2 : 3 : 4).

5. "Note on Volhard's method for the assay of silver bullion." By T. K. Rose, D.Sc.

The precautions to be observed in using the method are described, and the limit of accuracy put at 0·1 per 1000, instead of 0·25 per 1000, as stated by Van Riemsdyk.

6. "*c*-Substituted hydroxytriazoles." By George Young, Ph.D., and Ernest Witham, B.A., B.Sc.

The authors have prepared hydroxytriazoles by two actions represented by the equations $R{\cdot}CH{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2 + O = R{\cdot}C\langle\begin{smallmatrix}N{\cdot}NH\\ \\ N\end{smallmatrix}\rangle C{\cdot}OH + H_2O$, $R{\cdot}CHO + NH_2{\cdot}CO{\cdot}N{:}N{\cdot}CO{\cdot}NH_2 = R{\cdot}C\langle\begin{smallmatrix}HN{\cdot}N\\ \\ N\end{smallmatrix}\rangle C{\cdot}OH + NH_3 + CO_2$. Where R is the same group, the products of the two actions are apparently identical.

c-Phenylhydroxytriazole, $C_6H_5{\cdot}C_2N_3H_2O$, m. p. 321—322°. Forms two silver salts, $C_6H_5{\cdot}C_2N_3HO{\cdot}Ag$ and $C_6H_5{\cdot}C_2N_3O{\cdot}Ag_2$. Acetyl derivative, $C_6H_5{\cdot}C_2N_3HO{\cdot}C_2H_3O$, m. p. 248°. *c-Metanitrophenylhydroxytriazole*, $NO_2{\cdot}C_6H_4{\cdot}C_2N_3H_2O$, m. p. 304°. Forms two

silver salts, $C_8H_5N_4O_3Ag$ and $C_8H_4N_4O_3Ag_2$. Acetyl derivative, $C_8H_5N_4O_3\cdot C_2H_3O$, m. p. 261—262°. *Cinnamalsemicarbazone*, $C_6H_5\cdot CH{:}CH\cdot CH{:}N\cdot NH\cdot CO\cdot NH_2$, m. p. 215—216°. *c-Styrenylhydroxytriazole*, $C_6H_5\cdot CH{:}CH\cdot C_2N_3H_2O$, m. p. 311°. Forms two silver salts, $C_{10}H_8N_3OAg$ and $C_{10}H_7N_3OAg_2$. Monoacetyl derivative, $C_{10}H_8N_3O\cdot C_2H_3O$, m. p. 241—242°. Diacetyl derivative, $C_{10}H_7N_3O\cdot(C_2H_3O)_2$, m. p. 137—138°.

7. "**Note on the use of a mixture of dry silver oxide and alkyl halides as an alkylating agent.**" **By G. Druce Lander.**

Dry silver oxide and alkyl iodides have been employed in the preparation of the ethereal salts of alkyloxy-acids (*Trans.*, 1899, **75**, 157, 485, 754). The use of the method in the preparation of alkyl derivatives of compounds of other classes has been studied. Optically active ethyl menthyl ether has been prepared by the action of dry silver oxide and ethyl iodide on *l*-menthol. The optically active ether is an oil boiling at 207·5°—209·5° (uncorrected); d 20°/4° = 0·8537: $[\alpha]_D^{20°} = -98·32°$.

The ethyl and isopropyl ethers of benzoin are obtained by the action of silver oxide and ethyl and isopropyl iodides respectively on benzoin. The ethyl ether crystallises from light petroleum in needles melting at 58—58·5°; compare Limpricht and Jena (*Annalen*, 1870, **155**, 96), and Fischer (*Ber.*, 1893, **26**, 2415). The isopropyl ether, of similar crystalline form, melts at 72—75°.

The action of silver oxide and ethyl iodide on benzamide leads to the formation of ethyl benzimidoether. The hydrochloride melts at 119—120° with evolution of gas; compare Pinner (*Ber.*, 1883, **16**, 1654) and Tafel and Enoch (*Ber.*, 1890, **23**, 103).

The introduction of one ethyl group in place of hydrogen in ethyl acetoacetate can be readily effected by the aid of silver oxide and ethyl iodide. The product consists of ethyl ethylacetoacetate containing, however, approximately 2 per cent. of ethyl β-ethoxycrotonate, melting at 30°, and yielding on hydrolysis ethoxycrotonic acid which melts at 137·5°, with evolution of gas. The introduction of an ethyl group into ethyl ethylacetoacetate, and ethyl malonate by the same method is also possible, but the proportion of the ethyl homologue obtained is small. No indication could be obtained of the production of the ethyl homologue of ethoxycrotonic acid by the action of silver oxide and ethyl iodide.

Ethyl acetosuccinate may be prepared by the action of silver oxide and ethyl iodoacetate upon ethyl acetoacetate.

Further results and details will be given in a subsequent communication.

ADDITIONS TO THE LIBRARY.

I. Donations.

Coppock, J. B. Volumetric analysis; specially adapted to the requirements of students entering for the Advanced Practical Chemistry Examinations of the Science and Art Department, also the Intermediate Science and Preliminary Scientific Examinations of the University of London. London 1899. From the Author.

Henderson, G. G., and M. A. Parker. An introduction to analytical chemistry. London 1899. From the Authors.

II. By Purchase.

Berthollet, C. L. Essai de statique chimique. Two vols. Paris 1803.

Erdmann, H. Lehrbuch der Anorganischen Chemie. Braunschweig 1898.

Lachman, Arthur. The spirit of organic chemistry, an introduction to the current literature of the subject. With an introduction by Paul C. Freer. New York, 1899.

Pamphlets.

Hiortdahl, Th. Om hydrazinets sulfater og alun samt om dets bestemmelse ved overmangansur kali. Christiania 1897. From the Author.

Steuart, D. S.-S. The mineral wealth of Zoutpansberg: the Murchison Range gold-belt (excerpt from the Trans. of the Inst. of Mining Engineers). London 1899. From the Author.

Wardle, Sir Thomas. A paper on art as applied to the weaving and printing of textile fabrics. (Read before the Architectural Association, November 24, 1899.) From the Author.

Waterhouse, J. Teachings of daguerreotype (Traill Taylor Memorial Lecture III., 1899). From the Author

PROCEEDINGS OF THE ROYAL SOCIETY.

A few volumes of the above may be obtained by Fellows, in the order of application, from the Assistant Secretary, Chemical Society, Burlington House, W., at the price of 10*s.* per vol. Vols. 8–12, 15–24, 27, 37–45 are in stock.

At the next meeting, on Thursday, February 1st, 1900, the following papers will be communicated by the authors :—

"The chlorine derivatives of pyridine. Part V. Synthesis of *aa'*-dichloropyridine. Constitution of citrazinic acid." By W. J. Sell, M.A., and F. W. Dootson, M.A.

"The formation of heterocyclic compounds." By S. Ruhemann and H. E. Stapleton.

"The space configuration of quadrivalent sulphur derivatives. Methyl ethyl thetine dextrocamphorsulphonate and dextrobromocamphorsulphonate." By W. J. Pope and S. J. Peachey.

"Nitrocamphane." By M. O. Forster.

VICTOR MEYER MEMORIAL LECTURE.

The Victor Meyer Memorial Lecture will be delivered by Professor T. E. Thorpe, F.R.S., President of the Society, on the evening of Thursday, February 8th, 1900, at 8.30.

RICHARD CLAY AND SONS, LIMITED, LONDON AND BUNGAY.

Issued 6/2/19

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 16. No. 218.

February 1st, 1900. Professor Thorpe, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. Frank Curzon Britten, 21 Osbaldeston Road, London, N.; Robert Eadie, junr., 31 Clarendon Street, Partick, N.B.; Morris Broad Fowler, 30 West Park, Clifton, Bristol; Reginald Gordon Halstead, 3 Rathbone Place, Oxford Street, London, W.; James Henry Kershaw, 21 Richmond Park Road, Kingston-on-Thames; Thomas Macara, 6 West Bank Terrace, Hillhead, Glasgow; James Walter Tilley, 2 Stockwell Crescent, London, S.W.; Augustus John Walker, 3 Arnold Street, Hull.

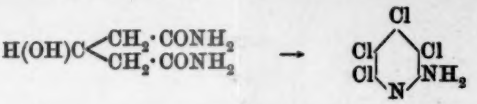
Of the following papers, those marked * were read.

***8. "The chlorine derivatives of pyridine. Part V. Constitution of citrazinic acid. Formation of $\alpha\alpha'$-dichloropyridine and of $\alpha\alpha'$-diiodoisonicotinic acid." By W. J. Sell, M.A., and F. W. Dootson, M.A.**

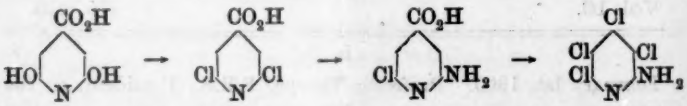
Although its genetic relationships leave little room for doubt that in citrazinic acid the hydroxyl groups occupy the $\alpha\alpha'$-positions relatively to the nitrogen, in view of the importance of this compound and its derivatives it was deemed expedient to obtain confirmatory evidence. This was done as follows:

The diamide of β-oxyglutaric acid was prepared and treated with

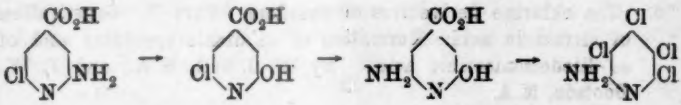
phosphorus pentachloride, when aminotetrachloropyridine was obtained. In this compound, the nitrogen atoms must be adjacent, thus:



By the action of phosphorus pentachloride on citrazinic acid, dichloroisonicotinic acid was obtained by Behrmann and Hofmann (*Ber.*, 1884, 17, 2694) and by the authors (*Trans.*, 1897, 71, 1069), and this interacts with ammonia to form aminochloroisonicotinic acid. (*Trans.*, 1897, 71, 1075), which substance, on further treatment with phosphorus pentachloride, loses its carboxyl group, and yields an aminotetrachloropyridine identical with that mentioned above. These changes may be represented thus:



In this way, the postition of one of the hydroxyl groups is shown. That both hydroxyl groups occupy the same relative position in the molecule is demonstrated by the following reactions: Aminochloroisonicotinic acid was treated with nitrous acid by a modification of Bouveault's method (*Trans.*, 1898, 73, 781), and chlorohydroxyisonicotinic acid obtained. This substance is identical with the product obtained by the action of soda on dichloroisonicotinic acid, as was shown by the melting point of the methyl ester. The acid, on treatment with aqueous ammonia, yielded a compound free from chlorine, which proved to be aminohydroxyisonicotinic acid, and by its interaction with phosphorus pentachloride the latter was converted into α-aminotetrachloropyridine, also identical with that mentioned above. These changes are thus shown:



The reduction of dichloroisonicotinic acid to isonicotinic acid by hydrogen iodide has been described by Behrmann and Hofmann (*loc. cit.*, p. 2696). The authors show that an interesting intermediate compound, diiodoisonicotinic acid, is produced.

By heating the silver salt of αα′-dichloroisonicotinic acid in a stream of carbon dioxide, αα-dichloropyridine was obtained. This compound

melts at 87—88°, and is identical with the dichloropyridine obtained by the interaction of pyridine and phosphorus pentachloride (*Trans.*, 1898, 73, 433).

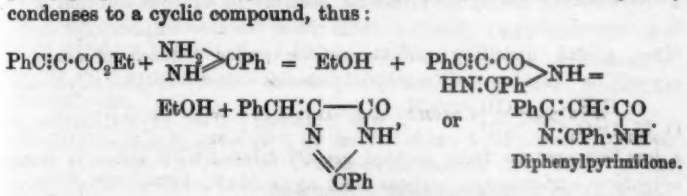
Discussion.

Dr. Ruhemann said that if the work of Behrmann and Hofmann left any doubt as to the position of the hydroxyl groups in citrazinic acid, it had been completely removed by the study of the action of ammonia on ethyl aconitate. The only explanation possible of this reaction was that ammonia effected the ring formation by condensing with the two carboxyl groups, and that the oxygen atoms in the citrazinamide thus were in the $\alpha\alpha'$-positions. Confirmatory evidence was given also by the formation, in an analogous manner, of the dicarboxylic acids derived from $\alpha\alpha'$-dihydroxypyridine.

Mr. Sell, in reply, pointed out that, although by no means minimising the value of proofs of constitution derived from methods of formation, especially where the yield was approximately theoretical, he was of opinion that where (as in the cases cited by Dr. Ruhemann) something like 80 per cent. of the materials are converted into substances as yet unidentified, it was most essential that independent and conclusive evidence should be brought forward.

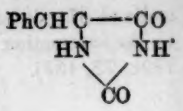
***9. "The formation of heterocyclic compounds." By S. Ruhemann and H. E. Stapleton.**

The authors have continued the investigation of the interaction of organic bases and ethereal salts of acids of the acetylene series, and have found that the action of bases on ethyl phenylpropiolate gives rise to heterocyclic compounds. In the case of benzamidine, when the reaction takes place at the temperature of the water-bath, besides the benzalphenylglyoxalidone previously described (Ruhemann and Cunnington, *Trans.*, 1899, 75, 954), *diphenylpyrimidone* is formed. This shows that benzamidine first reacts with the ethereal group of ethyl phenylpropiolate, forming a substituted amide, which subsequently condenses to a cyclic compound, thus:

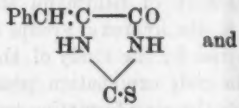


Benzal phenylglyoxalidone. Diphenylpyrimidone.

The compound formed with urea, previously described as a simple

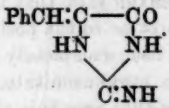
ureide, they now find to be benzalhydantoin, 

Similarly, thiourea and guanidine yield respectively,



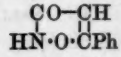
Benzal thiohydantoin.

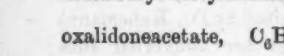
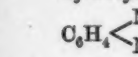
and



Benzal imidohydantoin.

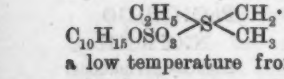
The constitution of these substances is proved by their giving α-hydroxycinnamic acid when boiled with potash.

The authors further show that the compound previously described as phenylpropiolohydroxamic acid, is α-phenyl-γ-isoxazolone 

With ethyl acetylenedicarboxylate, *o*-phenylenediamine gives ethyl quinoxalidoneacetate,  (m. p. 210°), which on hydrolysis loses carbon dioxide, giving methylquinoxalidone,  .

The authors found that ethyl propenetetracarboxylate (formed by the union of the ethyl salts of malonic and acetylenedicarboxylic acids) reacts with ammonia, giving ethyl αα′-dihydroxypyridine-βγ-dicarboxylate, which, on hydrolysis with hydrochloric acid, loses the $\beta \cdot CO_2H$ group, and yields citrazinic acid.

***10. "The space configuration of quadrivalent sulphur derivatives. Methylethylthetine dextrocamphorsulphonate and dextro-α-bromocamphorsulphonate." By William Jackson Pope and Stanley John Peachey.**

On treating methylethylthetine bromide in aqueous solution with the corresponding quantity of silver dextrocamphorsulphonate, filtering and distilling off the water under reduced pressure, a crystalline residue of *methylethylthetine dextrocamphorsulphonate*,  , was obtained; after crystallisation at a low temperature from alcohol greatly diluted with ether, it forms colourless, microscopic prisms melting at 115—117°. When pure, it is not hygroscopic, but is extremely soluble in water, alcohol, or acetone.

Methylethylthetine dextro-α-bromocamphorsulphonate,

$$C_{10}H_{14}BrOSO_3>S<\begin{matrix}C_2H_5\\CH_2\cdot CO_2H\\CH_3\end{matrix}$$

was prepared in a similar manner; it is sparingly soluble in cold acetone, and crystallises in silky white needles melting at 166—168°.

The molecular rotatory powers of these salts in dilute aqueous solution are the molecular rotatory powers of the optically active acid ions, so that the basic thetine group possesses no optical activity; no resolution of the asymmetric thetine into optically active components occurs, because more than one-half of the thetine bromide can be isolated as the pure optically active sulphonate. It is further most improbable that both salts are partially racemic and contain a dextro- and a lævo-thetine radicle, because partially racemic substances are of very rare occurrence.

The conclusion is drawn that, if sulphur really exists as a quadrivalent element in these salts, the four atoms directly and independently attached to the sulphur atom lie in the same plane as the latter, and that quadrivalent sulphur cannot lead to enantiomorphous configurations.

Previous attempts to prepare salts of asymmetric thetines and sulphonium compounds with optically active acids have invariably led to uncrystallisable products; the present are therefore the first observations from which information can be derived respecting the space configuration of quadrivalent sulphur compounds.

The investigation of these and allied substances is being continued.

***11. "Nitrocamphane." By M. O. Forster.**

The compound, $C_{10}H_{16}O_2NBr$, obtained by the action of potassium hypobromite on camphoroxime (*Trans.*, 1899, 75, 1141), is a *bromonitrocamphane*, $C_8H_{14}<\begin{matrix}CH_2\\|\\CBr\cdot NO_2\end{matrix}$, although it gives Liebermann's reaction for nitroso-derivatives.

Nitrocamphane, $C_8H_{14}<\begin{matrix}CH_2\\|\\CH\cdot NO_2\end{matrix}$, prepared by reducing bromonitrocamphane with alcoholic potash, melts at 147—148°, and has the specific rotatory power $[\alpha]_D$ +4·5° in alcohol; it gives Liebermann's reaction for nitroso-derivatives, and is indifferent towards alcoholic ferric chloride.

Pseudonitrocamphane, $C_8H_{14}<\begin{matrix}CH_2\\|\\C:N(OH):O\end{matrix}$, obtained on acidifying a solution of nitrocamphane in caustic potash, melts at 74°, and has $[\alpha]_D$ −95° (approximately); it develops a deep cherry-red coloration with ferric chloride, and changes spontaneously into the normal

modification either in the solid or dissolved state. In the latter condition, this transformation is accelerated by the influence of piperidine, alkalis, and sunlight. It forms a *potassium* derivative, a *benzoyl* derivative, and a *pseudo-nitrole*.

Chloronitrocamphane, $C_8H_{14}\begin{cases}CH_2\\CCl\cdot NO_2\end{cases}$, produced when sodium hypochlorite acts on camphoroxime, or when chlorine water is added to a solution of nitrocamphane in caustic alkali, melts at 217°, and has $[\alpha]_D$ −53·1° in alcohol; it gives Liebermann's reaction for nitroso-derivatives.

Iodonitrocamphane, $C_8H_{14}\begin{cases}CH_2\\CI\cdot NO_2\end{cases}$, precipitated from solutions of nitrocamphane in potash by iodine dissolved in potassium iodide, melts at 179°, and has $[\alpha]_D$ −10·8° in alcohol; it gives Liebermann's reaction.

Hydroxylaminocamphane (bornylhydroxylamine), $C_8H_{14}\begin{cases}CH_2\\CH\cdot NH\cdot OH\end{cases}$, prepared by reducing nitrocamphane with aluminium amalgam, crystallises from petroleum in small, oblong plates and melts at 154°; it dissolves in hot water, and the cold solution reduces ferric chloride, ammoniacal silver nitrate and Fehling's solution, almost immediately.

12. "The absorption spectra of ammonia, &c." By W. N. Hartley, F.R.S., and James J. Dobbie, D.Sc., M.A.

It was shown by Soret, and subsequently by Hartley and Huntington, that the purest forms of commercial ammonia which could be purchased (even that stated to be "volcanic ammonia"), contained some substance which exhibited an absorption band which was believed to be due to traces of some constituent of gas-liquor. There was distinct evidence that the band was due to an impurity (*Phil. Trans.*, Part I., 1879, p. 267). An aqueous solution of ordinary ammonia, 150 mm. in thickness, containing 2·5 grams ammonia in 100 c.c. gives a broad absorption band between 1/λ 3694 (λ 2707) and 1/λ 4306 (λ 2322). This band becomes less marked when the ammonia is converted into ammonium chloride, and this recrystallised repeatedly. It is altogether absent from ammonia prepared from ammonium oxalate which has been carefully purified by crystallisation. It is also absent from ammonia prepared by the reduction of hydroxylamine hydrochloride. The authors conclude, therefore, that the absorption shown by ordinary aqueous ammonia is due to an impurity which is not of inorganic origin, but is more probably due to pyridine bases. They have, in fact, found that ordinary strong ammonia is

contaminated with pyridine bases to the extent of about 0·00014 per cent.

They have measured also the continuous absorption of a normal solution of ammonia 200 mm. and 100 mm. in thickness. Methylamine hydrochloride and hydroxylamine hydrochloride show no selective absorption and are both highly diactinic. A solution of the former 150 mm. in thickness, containing 2·5 grams methylamine in 100 c.c. distilled water, shows practically no absorption, whilst a layer of the latter of the same thickness and strength transmits the whole spectrum with the exception of a few lines at the extreme violet end.

Acetaldoxime and acetoxime show considerable general absorption, but no selective absorption. A solution of acetaldoxime 150 mm. in thickness, containing 1·25 grams acetaldoxime in 100 c.c. of water, absorbs all lines beyond $1/\lambda$ 3323 (λ 3009); a layer 25 mm. in thickness of a solution containing 1 milligram-molecule dissolved in 20 c.c. of water gives a continuous spectrum to $1/\lambda$ 3952 (λ 2530). Acetoxime shows slightly greater absorption than acetaldoxime, due to the additional methyl group.

13. "Isoamarine." By Francis R. Japp, F.R.S., and James Moir, M.A., B.Sc.

In a recently published note (*Proc.*, 1899, **15**, 211), the authors showed that both ordinary amarine and the isoamarine of Snape and Brooke (m. p. 198°) have the structure $\begin{matrix} C_6H_5\cdot CH\cdot NH \\ C_6H_5\cdot CH\!-\!N \end{matrix}\!\!>\!C\cdot C_6H_5$, differing only in their configuration, the former being the meso-, the latter the racemic, form. The correctness of this view of the constitution of isoamarine was confirmed by the synthesis of this compound by heating *r*-diphenylethylenediamine with benzoic acid, and subsequently by its resolution into the enantiomorphs by Snape (*Proc.*, 1899, **15**, 228).

Feist and Arnstein, however, by heating *s*-dibenzoyl-*r*-diphenylethylenediamine in a current of gaseous hydrogen chloride, claim to have prepared an isoamarine melting at 175°, structurally identical with the foregoing (*Ber.*, 1895, **28**, 3177). As a third configuration —apart from those of the separate enantiomorphs, of which there can be no question here—is contrary to what theory predicts, we resolved to re-examine this compound.

We find that it melts at 198° instead of at 175°, and is in every respect identical with the isoamarine of Snape and Brooke.

The compound is so easy to purify that the wrong melting point given by Feist and Arnstein is doubtless a mere inadvertence.

14. "On the condensation of formaldehyde with ethyl malonate and on the synthesis of pentamethylenetricarboxylic acid." By J. Frank Bottomley and W. H. Perkin, jun.

In a previous communication by Haworth and Perkin (*Trans.*, 1898, **73**, 330), it was shown that the following substances are formed, either directly or indirectly, by the condensation of formaldehyde with ethyl malonate.

(1) *Ethyl methylenemalonate*, $CH_2{:}C(CO_2Et)_2$, and two polymerides called respectively ethyl *para*-methylenemalonate and ethyl *meta*-methylenemalonate. (2) *Ethyl propanetetracarboxylate*, $(CO_2Et)_2CH{\cdot}CH_2{\cdot}CH(CO_2Et)_2$. (3) *Ethyl tetramethylenetetracarboxylate*, $(CO_2Et)_2C<\begin{matrix}CH_2\\CH_2\end{matrix}>C(CO_2Et)_2$.

In the present paper, the authors show that, under certain conditions, *ethyl pentanehexacarboxylate*, $(CO_2Et)_2CH{\cdot}CH_2{\cdot}C(CO_2Et)_2{\cdot}CH_2{\cdot}CH(CO_2Et)_2$, is formed by the condensation of 3 mols. of ethyl malonate with 2 mols. of formaldehyde. This newester is crystalline, melts at 53—55°, and when digested with baryta, is decomposed with formation of an acid which is evidently propanetetracarboxylic acid, $(CO_2H)_2CH{\cdot}CH_2{\cdot}CH(CO_2H)_2$, since on heating at 240° it yields glutaric acid.

Pentanetricarboxylic acid, $CO_2H{\cdot}CH_2{\cdot}CH_2{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, is formed when ethyl hexacarboxylate is hydrolysed with dilute hydrochloric acid, and the resulting acid heated at 200°; it melts at 113—114° and has already been described by Emery (*Ber.*, 1891, **24**, 284). When ethyl pentanehexacarboxylate is heated with sodium ethylate and methylene iodide, it yields ethyl paramethylenemalonate, a remarkable decomposition which is discussed in the paper.

Ethyl pentamethylenehexacarboxylate, $(CO_2Et)_2{\cdot}\overset{\displaystyle CH_2\text{——}C(CO_2Et)_2}{\underset{\displaystyle C\cdot CH_2\cdot C(CO_2Et)_2}{|\quad\quad|}}$, is formed when the disodium compound of ethyl pentanehexacarboxylate is treated with bromine, and when hydrolysed yields *pentamethylene hexacarboxylic acid* (m. p. 212°). By the elimination of carbon dioxide from this acid, the *cis*- and *trans*-modifications of *pentamethylenetricarboxylic acid*, $\overset{\displaystyle CH_2\text{——}CH\cdot CO_2H}{\underset{\displaystyle CO_2H\cdot CH\cdot CH_2\cdot CH\cdot CO_2H}{|\quad\quad|}}$, have been prepared, the former melting at 146—148°, the latter at 127—130°. *Anhydro*-cis-*pentamethylenetricarboxylic acid*, $\overset{\displaystyle CH_2\text{——}CH\cdot CO}{\underset{\displaystyle CO_2H\cdot CH\cdot CH_2\cdot CH\cdot CO}{|\quad\quad|}}>O$, obtained by heating the *cis*-acid with acetic anhydride, melts at 215—217°, and when treated with water it is again converted into the *cis*-acid.

Experiments are also described on the distillation of the *para*- and

meta-polymerides of ethyl methylenemalonate, and on the hydrolysis of these polymerides and of ethyl methylenemalonate itself.

15. "The volumetric estimation of potassium." By R. H. Adie, M.A., and T. B. Wood, M.A.

The method proposed by the authors is to precipitate the potassium as cobaltinitrite (of which the formula is usually given as $K_6Co_2(NO_2)_{12}.3H_2O$ and to titrate the nitrite with a standard solution of potassium permanganate in acid solution. The experiments of the authors so far seem to show that there are three, instead of two, nitrite groups for each atom of potassium, and that the precipitate they obtain is probably an acid salt, as the ratio of the cobalt to the nitrite is that indicated by the above formula.

The method is as follows. The solution containing the potassium to be estimated is freed from other bases, as far as possible, by means of sodium carbonate, then concentrated if the solution is at all weak, acidified with acetic acid and excess of a solution of sodium cobaltinitrite added. The mixture is allowed to stand for 24 hours, the precipitate collected on a Gooch filter, washed several times with 10 per cent. acetic acid, and finally once with water. The asbestos filter and the precipitate are now transferred to a beaker, and boiled with a dilute solution of soda, filtered, and made up to 100 c.c. Of this solution 20 c.c. are taken, acidified with dilute sulphuric acid, and rapidly titrated with the permanganate solution. A second fraction of 20 c.c. is taken, and to this the amount just found of permanganate solution is added, then acidified, and the end point again determined. In one estimation, the volumes required were 16·3 and 16·4 c.c. respectively. The end of the reaction is more easily obtained if the permanganate is added to the nitrite solution in excess and the excess determined by potassium iodide and thiosulphate solution.

On testing the method with pure potassium salts, it was found that the results, whilst very concordant amongst themselves, gave results too high in almost exactly the proportion 3 : 2 ; 1 c.c. of the permanganate solution used was in this way found to correspond only to 0·0077 gram of K_2O instead of to 0·01175, the value calculated from the formula given above. This seems to indicate for the precipitated salt some formula such as $K_2HCo(NO_2)_6$.

As examples of the accuracy of the method the following analyses are given—

(I) Kainite :

	I.	II.	Mean.
K_2O per cent.....	12·22	11·94	12·13
By platinochloride method :			
K_2O per cent.....	11·98	12·07	12·03

(II) Commercial potassium sulphate:

	I.	II.	Mean.
K_2O per cent.....	50·05	50 82	50·44

By platinochloride method:

K_2O per cent.....	50·80

(III) Soil:

	I.	II.	III.	IV.	Mean.
K_2O per cent....	1·09	1·20	1·06	1·05	1·10

By platinochloride method:

1·11	1·25	0·98	0·97	1·08

The authors are engaged in making a more complete investigation of the composition of the precipitated cobaltinitrite and its decomposition by alkalis, as well as the application of the method to the determination of cobalt.

16. "On the action of aluminium chloride on camphoric anhydride. III." By F. H. Lees and W. H. Perkin, jun.

The authors have already published two notices of their work on the action of aluminium chloride on camphoric anhydride (*Proc.*, 1898, 14, 111, and 1899, 15, 23), and in spite of this, M. Blanc (*C. R.*, 1899, 129, 1019; *Chem. Centr.*, 1900, 1, 199) has lately undertaken an investigation of the new substances formed in this reaction which were first obtained by the authors, the examination of which was expressly reserved by them. The authors are therefore compelled to publish the results they have obtained, although the investigation is still incomplete.

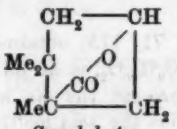
When camphoric anhydride reacts with aluminium chloride at ordinary temperatures, the principal product is *isolauronolic acid*, $C_9H_{14}O_2$, but there is also formed a lactone, $C_9H_{14}O_2$, called by the authors *ψ-campholactone*. This lactone, on hydrolysis with alkalis, yields two hydroxy-acids, $C_9H_{16}O_3$, which melt at 113° and 161° respectively (the melting points 109° and 152° previously given are too low).

When dissolved in a solution of hydrogen bromide in glacial acetic acid, ψ-campholactone is converted into a mixture of bromo-acids, $C_9H_{15}BrO_2$. One of these is liquid, but the other is a solid, melting at 128—130° with decomposition, which when boiled with glacial acetic acid loses hydrogen bromide with formation of an unsaturated acid, $C_9H_{14}O_2$ (m. p. 73°).

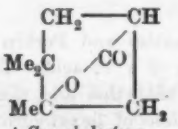
Attempts to reduce the solid bromo-acid with zinc dust and acetic acid led to the formation of a new lactone, $C_9H_{14}O_2$, which melts at 44°, and when hydrolysed with baryta water is converted into the same hydroxy-acid, $C_9H_{16}O_3$ (m. p. 113°), which is obtained by the hydrolysis of ψ-campholactone.

Probably ψ-campholactone and this new lactone are stereoisomeric, and the same remark applies to the two hydroxy-acids melting at 113° and 161°.

It was stated in one of the previous communications (*Proc.*, 1899, 15, 23) that, when ψ-campholactone is treated with phosphorus pentabromide and the product poured into methyl alcohol, *methyl bromodihydro-ψ-lauronolate* is obtained, and that this methyl ester, on hydrolysis, yields an oily unsaturated acid, $C_9H_{14}O_2$, called *ψ-lauronolic acid*. Since the publication of these results, it has been found that this oily acid, on standing for some weeks, deposits crystals which melt at about 69°, and it is evident that the oily acid is a mixture of two isomeric acids, $C_9H_{14}O_2$, which again are probably stereoisomeric. It was also suggested (*Proc.*, 1899, 15, 24) that campholactone and ψ-campholactone are possibly closely related, and that this relationship might be represented as follows:

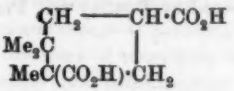


Campholactone.



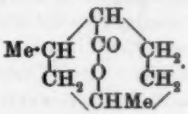
ψ-Campholactone.

these expressions being based on the formula



which is one of those suggested by Perkin as possibly representing the constitution of camphoric acid.

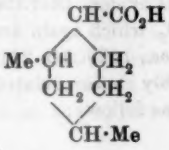
When, however, it is remembered that ψ-campholactone, dissolved in concentrated sulphuric acid, is almost quantitatively converted into xylic acid at 90°, and that, as has since been found, ψ-lauronolic acid yields the same acid on prolonged treatment with sulphuric acid at ordinary temperatures, it seems possible that ψ-campholactone may after all be the lactone of *hydroxyhexahydroxylic acid.*



It will be very difficult to prove whether ψ-campholactone is a 5 or 6 ring derivative, since experiments which were made on a considerable scale, with the object of reducing ψ-lauronolic acid—in which case either dihydroisolauronolic acid or hexahydroxylic acid should have

resulted and could have been identified—failed owing to the fact that ψ-lauronolic acid is not appreciably attacked even by repeated and prolonged treatment with amyl alcohol and sodium.

When a chloroform solution of camphoric anhydride is left for some weeks in contact with aluminium chloride, the ψ-campholactone remains unchanged, but the isolauronolic acid almost entirely disappears and in its place two saturated acids, $C_9H_{16}O_2$, are found; these have now been separated partly by freezing and partly by means of their crystalline amides. One of these acids is solid, melts at 77°, and is identical with the *hexahydroxylic acid*,



which Bentley and Perkin (*Trans.*, 1897, 71, 173) obtained by the reduction of xylic acid. The other acid, $C_9H_{16}O_2$, is an oil and it is probable that this and the solid acid represent the *cis-* and *trans-*modifications of hexahydroxylic acid. When the acid melting at 77° is treated with bromine and subsequently with alcoholic potash, it yields a solid acid, $C_9H_{14}O_2$ (m. p. 107°), which is identical with the *tetrahydroxylic acid* prepared by Bentley and Perkin (*loc. cit.*).

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE NEXT BALLOT.

The following Candidates have been proposed for election. A ballot will be held on Thursday, February 15th, 1900.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

Baker, Captain Frederick Nolan,

The Officers' Mess, 3rd Royal Inniskilling Fusiliers, Mullingar.

Late Assistant Master, Stationers' Company's School, London, N., and late Lieutenant, Reserve of Officers; second in command of the G.N.R. Detachment R.E. (Railway Reserve). (Student at Finsbury Technical College.) *a*, Personal interest in the progress of Chemical science; *b*, to obtain the advantage of perusing the Society's publications, and to enjoy the privilege of attending the meetings and using the Library. Among minor qualifications may be mentioned: *a*, the possession of "the Officers'" "Extra" (or Honours) Certificate from the School of Musketry, Hythe, which involves a complete knowledge of the mechanism of small arms and machine guns, and a theoretical and practical acquaintance with the properties of ammunition for the same (this qualifies for a Staff appointment); *b*, the possession of the "P.S." certificate in military engineering from School of Military Engineering, Chatham, in connection with which was a searching examination on the nature and constituents of the nitroglycerine compounds and other explosives largely used in war (qualifies for Staff appointment as Instructor of Engineering).

R. Meldola. Thomas J. Underhill.
Arthur J. Chapman. Gerald T. Moody.
William Jackson Pope.

Bennett, Alexander Hutcheon,

61, London Road, Bromley, Kent.

Analytical Chemist. Studied at Dulwich College and at Technical College, Finsbury. Chemist to Messrs. J. B. Lawes and Co.'s tartaric

and citric acid works, Millwall, for last 7 years. Engaged in research in conjunction with Mr. Brereton Baker.

John Bennet Lawes.	R. Meldola.
R. Warington.	*J. Henry Gilbert.*
H. Brereton Baker.	*Frank Clowes.*

Cole, Oscar Joseph (B.A., Lond.),
Wivenhoe, Colchester, Essex.

Teacher. Science Master, since January, 1898, at West Monmouthshire School, Pontypool. For 3 years previous to January, 1898 (from 1895 to end of 1897), Assistant Science Master at the Grammar School, Carlisle. Being anxious to keep pace with the progress of Chemistry and Chemical discovery.

E. P. Perman.	Harry P. Hodgson.
L. Hansen Bay.	*William Briggs.*
Thos. A. Shegog.	*Thomas Edwards.*

Cooper, William Francis,
Ashlyns Hall, Berkhampsted.

B.A., Clare College. Student of Chemistry.

W. J. Sell.	T. B. Wood.
H. J. H. Fenton.	F. W. Dootson.

W. T. N. Spivey.

Davison, Thomas Cuthbert,
49, Victoria Road, New Swindon, Wilts.

Analytical Chemist. At present Assistant to Mr. F. W. Harris, F.C.S., F.I.C., Chief Chemist to the Great Western Railway Co., and Teacher of Practical Chemistry in the Evening Classes at the Swindon and North Wilts. Technical School. The former position held for 8 years and the latter for 6 years.

F. W. Harris.	J. H. B. Jenkins.
W. R. Bird.	T. Judge.

L. Archbutt.

Dawson, Harry Medforth,
Yorkshire College, Leeds.

Demonstrator of Chemistry in the Yorkshire College, Leeds. Late 1851 Exhibition Science Scholar. "On the Conductivity of Flames containing Salt Vapours" conjointly with Professor Smithells and Mr. H. A. Wilson (*Phil. Trans. Roy. Soc.*, 193, p. 89); "On the Lowering of the Melting Point of Magnesium Chloride Hexahydrate by addition of Foreign Substances," with Prof. van't Hoff (*Zeit. Phys. Chem.*, 22, 598); "On Magnesium Sulphate with 1¼ Molecules of

Water of Crystallisation," with Prof. van't Hoff (*Berichte der Akad. der Wissenschaften Berlin*, 1899); "On the Racemic Transformation of Ammonium Bimalate" conjointly with Prof. van't Hoff (*Berichte*, 31, 528, *Jahrgang* 1898); "On the Influence of Pressure on the Formation of Tachyhydrite" (Inaugural Dissertation for the Degree of Ph.D. at Giessen), &c. Five years study of Chemistry at the Yorkshire College, Leeds. Three years study of Chemistry at Berlin, Leipzig, and Giessen. Degrees of Ph.D. and B.Sc. (Lond.).

Arthur Smithells. Herbert Ingle.
J. B. Cohen. Henry R. Procter.
J. McCrae.

Dixon, Stephen M.

University, Fredericton, N.B., Canada.

Professor of Civil Engineering, Assoc. M. Inst. C.E. B.A., B.A.I., Senior Moderator and Gold Medallist in Experimental Physics and Chemistry of the University of Dublin. Devoted much attention to Analyses of Ores, Rocks, &c.

J. Emerson Reynolds. Augustus E. Dixon.
Emil A. Werner. Richard J. Moss.
Robert Elliott Doran.

Findlay, Alexander,

Emilienstrasse 10', Leipzig, Germany.

1851 Exhibition Scholar. Master of Arts, and Bachelor of Science of Aberdeen University; for one and a half years (1896–1898) Private Assistant to Professor F. R. Japp, F.R.S.; in 1898, elected to an Exhibition (1851) Scholarship, and since then engaged in Research in the Physico-Chemical Institute of Leipzig University. Joint author with Professor Japp of "Phenanthrone" (*Trans.*, 1897); "Condensations of Anhydracetonebenzil and its Analogues with Aldehydes" (*Trans.*, 1899); "Triphenyloxazolone" (*Trans.*, 1899).

F. R. Japp. James Hendrick.
T. S. Murray. James Walker.
Fred W. Skirrow.

Foulds, James,

5, Murray Street, Burnley, Lancashire.

Chemical Master at the Public Higher Grade School, Blackburn. An Associate of the Royal College of Science, London. Late Exhibitioner at the Royal College of Science, London. Late Chemical Master, Wellington College, Salop. Late Chemical Master under the County Council, Salop. Late Chemist to Robertsons, Food Specialists, Manchester.

T. E. Thorpe. Chapman Jones.
W. Palmer Wynne. Barker North.
Sydney Whalley.

Gee, Granville Reginald,

Falcon Villa, Howard Street, Gloucester.

Analytical Chemist. Articled 5 years with G. Embrey, Esq., Public Analyst, City and County of Gloucester. Various successes in S. and A. Dept. Exams., including Queen's Prize (1st on list), Pract. Inorg. Chem., 1892, and 2nd Class Honours, 1894. Studentship at Royal College of Science, 1895—1896. Assistant to Messrs. R. R. Tatlock and Readman, Analytical Chemists, Edinburgh, 1897. Engaged by The Wednesfield Chemical Syndicate to carry out Experimental and Research work in electro-chemical manufacture, 1897—1898, then recalled to Edinburgh.

George Embrey. G. H. Gemmell.
William A. Tilden. George McGowan.
William Ramsay.

Geldard, Julius,

120, Park Field Terrace, Otley Road, Bradford.

Dyeworks Chemist, Messrs. Geo. Armitage, Ltd., Water Lane, Bradford. Three years Dyeing and Chemical Training at the Yorkshire College. One year Original Research with A. G. Perkin, F.C.S., F.R.S.E., with whom I published a paper in your Journal in 1895. Three years at Geo. Armitage, Ltd., as Analytical Chemist, during which I have done a great amount of coal analysis with relation to economy in steam raising.

J. J. Hummel. Arthur Smithells.
A. G. Perkin. Walter M. Gardner.
Walter Leach.

Gray, Robert W.,

7, Orme Court, Bayswater.

Student. Three years Student in Chemical Laboratory, University College, Gower Street. Tufnell Scholar.

William Ramsay. Alex. M. Kellas.
Morris W. Travers. Edward C. Cyril Baly.
S. Smiles.

Harvey, Alfred William,

13, Pendrell Road, St. Catherine's Park, Hatcham, S.E.

School Teacher. Joint author of paper entitled "The Homogeneity of Dextrolævo-α-phenethylamine Dextrocamphorsulphonate" (*Trans. Chem. Soc.*, 1899, p. 1110).

William Jackson Pope. Walter C. C. Pakes.
Stanley John Peachey. Arthur R. Ling.
Gerald T. Moody.

Hart, Herbert William,

13, Lynwood Villas, Darwen, Lancashire.

Chief Chemist to the Wall Paper Manufacturers, Limited (late Messrs. C. & J. G. Potter). I studied Chemistry during four years with Messrs. Crace Calvert and Thomson of Manchester, and acted as Assistant to them. Subsequently I held the position of Chemist to the Rossendale Printing Company for four years, where I carried out original investigations in Bleaching, Printing, and Dyeing Processes. Since 1895 I have been chief Chemist to Messrs. C. & J. G. Potter, conducting experiments and supervising the Chemical operations involved in Paper Making and Staining, and in the Recovery of Soda on a large scale from waste Esparto liquors.

William Thomson. C. F. Cross.
James Porter Shenton. *Thomas Fairley.*
Harry Bowes. *Geo. Ward.*

C. Estcourt.

Houston, Adam,

Brisbane House, Bellahouston, Glasgow.

Chemist. Two years Student with Dr. J. Clark, City Analyst, Glasgow, &c. One Session: Glasgow and West of Scotland Technical College.

G. G. Henderson. James Robson.
John Clark. Matthew A. Parker.

Thomas Gray.

Hutchin, Henry William,

Basset Road, Camborne.

Science Teacher. Three years in Messrs. Chance's Laboratory, Alkali Works, Oldbury, concurrently with tuition in Chemistry and Metallurgy by Messrs. Woodward and Hiorns at the Birmingham and Midland Institute. Two and a half years Chemist in charge at Messrs. Riley and Sons' Chemical Works, Lancashire. Three years Associateship Course, and 1 year as Teaching Scholar at South Kensington. Subsequently 3 years as Teacher in the Camborne School of Mines.

William A. Tilden. John J. Beringer.
W. Palmer Wynne. Gilbert T. Morgan.

John Gill.

Jackson, Henry,

Downing College, Cambridge.

B.A. (Cantab), B.Sc. (London), Fellow of Downing College, Cambridge. Assistant Demonstrator of Chemistry in the University Chemical Laboratory, Cambridge. Joint author with H. J. H. Fenton, M.A., F.R.S., "Oxidation of Polyhydric Alcohols in Presence of Iron" (*J. C. S.*, 1899, p. 1), "Crystalline Glycollic Aldehyde"

(*J. C. S.*, 1899, p. 575); with W. J. Sell, M.A., F.I.C., "Synthesis of some Derivatives of $\beta\beta'$-Dipyridyl from Citrazinic Acid" (*J. C. S.*, 1899, p. 507).

H. J. H. Fenton. T. B. Wood.
W. J. Sell. W. T. N. Spivey.
W. H. Mills.

Joyce, Thomas Goode,
The Smallthorns, Stafford.

Analytical Chemist. B.Sc. (Lond.), A.I.C. Associate of the Mason University College, Birmingham. Chemist in the Laboratories of Messrs. Blackwell, Hayes, and Spilsbury, Birmingham.

Percy F. Frankland. W. R. Innes.
C. F. Baker. James Spilsbury.
Godfrey Melland.

Kynaston, William Charles Robert,
9, Harland Road, Higher Tranmere, Birkenhead.

Student of Chemistry. Four years (1894—1898) articled pupil to Messrs. Edward Davies and Son, Analytical and Consulting Chemists, The Laboratory, 28, Chapel Street, Liverpool. Twelve months (1898—1899) Student in the Honours School of Chemistry, Owens College, Manchester.

Edward Davies. William A. Bone.
Francis Henry Tate. Edward J. Russell.
H. B. Dixon.

Laws, Arthur Robert,
48, Waverley Terrace, Newcastle-on-Tyne.

Senior Science Master at the Royal Grammar School, Newcastle. Past Student of the Durham College of Science. Undergraduate, London University. Senior Science Master, Royal Grammar School, Newcastle. Consulting Chemist to Tyne Metal Works, &c.

R. Phillips Bedson. *F. J. Lloyd.*
Saville Shaw. *E. G. Clayton.*
F. C. Garrett. *Wm. Chattaway.*

Mackenzie, Thomas Ebenezer,
6, Cardonald Park Terrace, Cardonald, near Glasgow.

Technical Chemist. Ten years Chemist in the Tharsis Company's Laboratory in Glasgow. Three years Chemist at the Tharsis Mines, Spain. Five years Chemist at the Dalzell Steel Works, Motherwell. Four years Assistant to Mr. J. S. MacArthur. Technical Chemist.

Now Technical Manager of the North British White Lead Company, Limited.

John S. MacArthur.	John Clark.
R. R. Tatlock.	*Edmund J. Mills.*
R. T. Thomson.	*G. H. Gemmell.*

Mair, William,

388, Morningside Road, Edinburgh.

Chemist on the staff of the North London Chemical Works (Fletcher, Fletcher & Co.). 1892—1893: Extra-Mural Teacher in Practical Materia Medica and Pharmacy, recognised by the University of Edinburgh, for University College, Dundee, at Dundee Royal Infirmary. 1892—1893: Course of study in Practical Analytical Chemistry: at University College, Dundee, Inorganic and Organic; Winter and Summer Day Sessions; Professor Percy F. Frankland, F.R.S. 1893: University College, Dundee, Lectures in Organic Chemistry; Professor Percy F. Frankland, F.R.S. 1892—1893: Research Work in Clinical Chemistry at Dundee Royal Infirmary. 1893: Author of "Pharmacopœia of Dundee Royal Infirmary," 12mo, pp. 94 (in use at Dundee Royal Infirmary, 1899). 1896: Joint author, with Rai Kanai Lall Dey, Bahadur, C.I.E., F.C.S., formerly Professor of Chemistry in Medical College, Calcutta, of "Indigenous Drugs of India" (Pharmacological and Chemical), 8vo, pp. xl, 387.

Fred W. Fletcher.	Percy F. Frankland.
Peter MacEwan.	*M. Carteighe.*
Frank W. Young.	*Wyndham R. Dunstan.*

Thomas Tyrer.

Menzies, Alan W. Cranbrook, M.A., B.Sc.,

11, Howe Street, Edinburgh.

Lecturer in Chemistry. Graduated at Edinburgh, Arts 1897, Science 1898. Assistant Professor of Chemistry, Heriot-Watt College, Edinburgh. "Vans Dunlop" Scholar in Chemistry, Edinburgh University.

Alex. Crum Brown.	Leonard Dobbin.
J. Gibson.	Hugh Marshall.

John S. Lumsden.

Morgan, John Livingston Rutgers,

47, Bayard Street, New Brunswick, New Jersey, U.S.A.

Tutor in Chemical Philosophy and Chemical Physics, Columbia University, New York City. B.Sc. Rutger's College, 1892. A.M. and Ph.D. University of Leipzig, 1895. Author of "Die Bestimmung von Cyaniden auf elektrometrischem Wege" (*Zeit. für physikalische*

Chemie, 17, 513—536); with A. H. Gotthelf, "The Theory of the Formation of Nickel Sulphide" (*Jour. Am. Chem. Soc.*, 21, 494—503); "The Theory of the Separation of Barium, Strontium, and Calcium from the mixed Sulphates" (*Jour. Am. Chem. Soc.*, 21, 522—527); "Three Additions to the Kohlrausch-Ostwald Conductivity Method" (*Jour. Am. Chem. Soc.*, 21, December). Books: *The Principles of Mathematical Chemistry*, from the German of Georg Helm (New York: 1897); *An Outline of the Theory of Solution, and its Results* (New York: 1897); *The Elements of Physical Chemistry* (New York: 1899).

C. F. Chandler. Samuel Auchmuty Tucker.
Jas. S. C. Wells. Peter T. Austen.
Marston Taylor Bogert.

Morris, Edgar Ford,

69, Shrewsbury Street, Old Trafford, Manchester.

Works Chemist. M.A., Oxford, with Honours in Chemistry formerly Demonstrator in Balliol College Laboratory, Oxford.

John Conroy. A. F. Walden.
D. H. Nagel. J. E. Marsh.
William E. Moss.

Morris, Herbert Newall,

48, Lansdowne Road, Crumpsall, Manchester.

Technical Chemist. Student at Owens College under Schorlemmer, and Zürich University under Merz. For the last six years Works Chemist for Messrs. Levinstein, Ltd. Publication on "Vapours from Heated Sulphuric Acid" (*J. C. I.*, 1898).

G. H. Bailey. W. H. Bentley.
C. Estcourt. Alex. K. Miller.
Jno. Hübner.

Naylor, Ernest Brooks,

73, Castle Street, Bolton.

Science Master. Student during 4 years in the Owens College. Honours B.Sc. in Chemistry (Victoria University) 1898. Science Master (Chemistry and Physics), School of Science, Burnley.

H. B. Dixon. W. T. Lawrence.
W. H. Perkin, jun. D. L. Chapman.
E. J. Russell.

Readman, James Fraser,

50, Jane Street, Glasgow.

Technical Chemist. Two years Assistant Chemist to the Steel Co. of Scotland, Ltd. Nine and a-half years Chemist to the Butterley Co., Butterley, Derbyshire. Two years Chemist to the Parkgate Iron

and Steel Co., Ltd., Rotherham. Five years Chemist and Steel Furnace Manager to the New British Iron Co., Ltd., Cradley Heath, Staffordshire. Two years in present situation as Assistant to Mr. J. S. MacArthur, Technical Chemist, Glasgow.

John S. MacArthur.	G. H. Gemmell.
R. R. Tatlock.	*Edmund J. Mills.*
R. T. Thomson.	*John Clark.*

Riley, Walter A.,

Brunswick Lodge, Newmarket Road, Norwich.

Brewer and Brewers' Chemist. Two years with Mr. John Heron, F.I.C., studying Pure and Applied Chemistry. Two and a-half years in Lager Beer and other breweries. Member Institute of Brewing, Member Society of Chemical Industry. Am at present Assistant Chemist in Brewers' Laboratory.

John Heron.	B. E. R. Newlands.
Francis Sutton.	*F. J. Lloyd.*
Otto Hehner.	*John R. Skelton.*
Arthur R. Ling.	*F. Napier Sutton.*

Sanders, James McConnell,

37, Summerhill Road, Dartford.

Works Chemist. Late Natural Science Scholar, University of Wales. For two years Assistant Science Master, Eastbourne College. For one year Assistant to Mr. C. J. Wilson, F.I.C., F.C.S. For past two years Chemist at Messrs. Burroughs, Wellcome & Co.'s Works, Dartford.

H. Lloyd Snape.	W. C. Reynolds.
Charles J. Wilson.	Francis H. Carr.

H. A. D. Jowett.

Sargeant, Fred Pilkington,

Springfield Place, Leeds.

Teacher of Chemistry, &c. Applicant was for seven years Pupil of, and Assistant to, Mr. J. T. Brierley, Lecturer on Chemistry at the Chorley Science School; he then underwent a full course of instruction in Chemistry, &c., at the Manchester College of Pharmacy, afterwards holding the post of Assistant Lecturer for nearly two years. He has been Principal of the Leeds College of Pharmacy for the last twelve months, during which time he has also held the posts of Demonstrator in Pharmacy and Toxicology at the Medical School of the Yorkshire College. He holds First Class Certificates in Practical and Theoretical Chemistry (Science and Art Department), and the Minor

and Major Certificates of the Pharmaceutical Society. He is author of "Notes on Estimation of Chloral Hydrate" (*Ph. J.*, 4, 9, 236).

Jno. T. Brierley. Frederick W. Branson.
T. Armistead Ward. *C. Sordes Ellis.*
Arthur Smithells.

Smith, Edward Shrapnell,

35, Botanic Road, Wavertree Park, Liverpool, E.

Chemical Engineer, Memb. San. Inst., Memb. Soc. Chem. Ind. At present on the technical staff of The United Alkali Co., Ltd. For six years Head Chemist on the Deacon Chlorine Plant at Gaskell and Deacon's Works, Widnes, 1893 to 1899. Now transferred to Head Office, Technical Department for Investigation of Processes at Consumers' Works in various parts of the country. Only published work, "Some Notes on the Disinfection and Deodorisation of Sewage by Chlorine" (*Jour. Soc. Chem. Ind.*, June, 1898), "Some Experiments upon High-strength Hypochlorite Solutions" (*Jour. Soc. Chem. Ind.*, December, 1898, and March, 1899).

Edward Davies. Boverton Redwood.
George Tate. David L. Salomons.
William Naylor.

Hart-Smith, James,

4, Edenvale Street, Fulham.

Student Teacher in Chemistry, Royal College of Science. Associate of the Royal College of Science in Chemistry. Associate of the Institute of Chemistry.

William A. Tilden. Chapman Jones.
W. Palmer Wynne. M. O. Forster.
G. T. Morgan.

Storr, Bertram Vincent,

17, York Road, Ilford, Essex.

Assistant Chemist, Britannia Works, Ilford. For 4 Sessions (1894—98) a Student at the Yorkshire College, Leeds, taking B.Sc., Vict., with Honours in Chemistry; Priestley Research Scholar at Mason College, Birmingham, 1898—1899; now Research Chemist as above.

Arthur Smithells. Percy F. Frankland.
J. B. Cohen. C. F. Baker.
F. F. Renwick.

Strong, Archie Hugh,

Stoneleigh Villa, 63 Herne Hill Road, Camberwell, S.E.

Analytical Chemist and Assayer. Ten years experience in Analytical

Chemistry, including six years experience as sole Chemist on a Pyrites Mine in Pilley's Island, Newfoundland.

Edw. Riley. F. W. Daw.
James E. Ferguson. Robt. D. Connell.
Isaac S. Scarf.

Waterhouse, Gustavus Athol, B.Sc.,
"Ellerslie," Birrell Street, Waverley, New South Wales.

Student at the Sydney University. Four years of study at the Sydney University, more or less continuously in the Chemical Laboratory. Obtained degree of Bachelor of Science in 1899. At present in the third year of the Mining and Metallurgy course.

A. Liversidge. Basil Turner.
J. A. Schofield. C. Walker.
F. B. Guthrie. *John C. H. Mingaye.*
Thos. Steel.

Wilson, Leonard Philip,
123, Chadwick Road, East Dulwich, S.E.

Student. Associate of the City and Guilds Institute. Leathersellers' Research Fellow at the Central Technical College.

Henry E. Armstrong. William A. Davis.
Gerald T. Moody. T. M. Lowry.
William J. Pope.

Authorised by Council, Bye-Law I, (3).

Calvert, Sidney,
Missouri State University, Columbia, Missouri.

Assistant Professor of Chemistry. B.Sc. (1st Class Honours) McGill University, Montreal, 1890. Student Graduate School of Harvard University, 1890—1894. A.M., *ibid.*, 1892. Assistant in Chemistry, *ibid.*, 1892—1894, and private Research Assistant to Prof. C. Loring Jackson, 1892—1894; with C. L. Jackson, "Bromine Derivatives of Metaphenylenediamine" (*Proc. Am. Acad.*, 1894); with same, "On the behaviour of certain derivatives of Benzol containing Halogens" (*Proc. Am. Acad.*, 1894). Appointed Assistant Professor of Chemistry, Missouri State University, 1894. With H. B. Gibson and D. W. May, "Dietary Studies at the University of Missouri, 1895," &c. (U.S. Department of Agriculture, Bulletin No. 31, 1896).

B. J. Harrington. Chas. Baskerville.
W. G. Brown. F. P. Venable.

PROCEEDINGS OF THE ROYAL SOCIETY.

A few volumes of the above may be obtained by Fellows, in the order of application, from the Assistant Secretary, Chemical Society, Burlington House, W., at the price of 10*s.* per vol. Vols. 8–12, 15–24, 27, 37–45 are in stock.

VICTOR MEYER MEMORIAL LECTURE.

The Victor Meyer Memorial Lecture will be delivered by Professor T. E. Thorpe, F.R.S., President of the Society, on the evening of Thursday, February 8th, 1900, at 8.30.

At the next ordinary meeting, on Thursday, Feb. 15th, there will be a ballot for the election of Fellows, and the following papers will be communicated :—

"Ammonium amidosulphite." By Edward Divers and Masataka Ogawa.

"Products of heating ammonium sulphites, thiosulphates, and trithionate." By Edward Divers and Masataka Ogawa.

"Note on the refraction and magnetic rotation of hexamethylene." By S. Young, D.Sc., F.R.S., and Emily C. Fortey, B.Sc.

"The combination of sulphur dioxide and oxygen." By Edward J. Russell and Norman Smith.

"Note on the estimation of gases containing sulphur." By E. J. Russell.

"Apiin and Apigenin. II. Note on Vitexin." By A. G. Perkin.

"The yellow colouring principles of various tannin matters. VII." By A. G. Perkin.

RICHARD CLAY AND SONS, LIMITED, LONDON AND BUNGAY.

Issued 22/2/1900

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 16. No. 219.

February 8th, 1900. Extra Meeting. Sir HENRY ROSCOE, LL.D., F.R.S., Vice-President, in the Chair.

The President, Professor T. E. THORPE, LL.D., F.R.S., delivered the Victor Meyer Memorial Lecture.

Victor Meyer was born in Berlin on September 8th, 1848, and died in Heidelberg on August 8th, 1897. He was at the time of his death President of the German Chemical Society, and had been an Honorary Foreign Member of the Chemical Society since 1883. As a friend of nearly 30 years' standing, and as one who studied with him under Bunsen, the President had acceded to the request of the Council to record its appreciation of the remarkable services Victor Meyer rendered to the science which he cultivated during the all too short period of his activity with such striking assiduity and success.

Some account was given of Meyer in his student days in Heidelberg, of his early connection with the University Chemical Society, and of his work as one of Bunsen's assistants. In 1868, he entered Baeyer's laboratory at the Gewerbeakademie in Berlin, and began the series of half-dozen investigations which characterised his activity during his three years' stay in the German capital. Special reference was made to his memoir on the constitution of the disubstituted benzenes, and upon his method of introducing a carboxyl group into the molecule of aromatic compounds by the action of sodium formate upon the potassium salt of the aromatic sulpho-acids, and it was shown how the results of his observations led to a revision of the views then held with respect to the orientation of the radicles in the "ortho" and "meta" (salicylic) series.

Meyer's success as a private teacher induced von Baeyer to recommend him to Fehling, who sought assistance, especially in the teaching

of modern organic chemistry and in practical work in connection with his duties at the Stuttgart Polytechnic. Although he remained in Stuttgart barely a year, he there made one or two discoveries, especially that of the nitro-compounds of the fatty series, which at once stamped him as an original investigator of a very high order. From Stuttgart he was called to Zürich as the successor of Wislicenus, who had been moved to Würzburg, and, when barely 24 years of age, he was elected Ordinarius and Director of the chemical laboratory of the Polytechnic. The 13 years of Meyer's stay at Zürich constitute the most fruitful and the most brilliant period of his career; before its close he had brought himself within the foremost rank of contemporary investigators. Some idea of his wonderful power of work, and of the stimulus he gave to others, may be gleaned from the fact that during that period the Zürich Laboratory gave close on 130 papers and memoirs to chemical literature. Special stress was laid upon the elaborate investigation of the nitro-compounds of the alkyl series and their derivatives, which continued to occupy Meyer and his pupils for many years. Reference was made to the discovery of the nitrolic and azaurolic acids, and of the pseudonitroles, and it was pointed out how the characteristic colour reactions afforded by the behaviour of nitrous acid with the primary and secondary nitro-paraffins, and its inability to act upon the tertiary compounds, offered a ready means of distinguishing primary, secondary, and tertiary alcohol radicles. It was shown how the same line of inquiry led to the discovery of the group of the azines and of the ketoximes and aldoximes, and what the influence of these discoveries was upon the stereochemistry of nitrogen.

It was at Zürich that Meyer devised his various methods of determining vapour densities, and it was pointed out what an important influence the simple and extremely convenient process, known as the air displacement method, has had upon our knowledge of the true molecular weights of substances. Meyer's work on the dissociation of the halogens was especially referred to. Pyrochemical problems, in fact, continued to interest him to the end, and he was quick to take advantage of any hint which seemed to promise the possibility of their solution. In a lecture before the Naturforscher Versammlung in Heidelberg, he regretted that the lack of vessels of sufficiently refractory material prevented him from working at the higher limits of temperature even then attainable. "There can be no doubt," he said, "that new and undreamt-of discoveries will manifest themselves —that a new chemistry will disclose itself—when we are furnished with vessels that will enable us to work at temperatures at which water can no longer exist, and at which oxyhydrogen gas becomes an uninflammable mixture."

In the autumn of 1882, Meyer was requested to undertake the delivery of the series of University lectures on benzene derivatives which had been interrupted by his friend Weith's death. It was in the course of these lectures that he came upon what is, perhaps, the most brilliant of all his discoveries—that of thiophen. He desired to show his class the indophenin reaction of Baeyer, which, at that time, was held to be indicative of benzene; but, to his astonishment, not a trace of the characteristic blue colour made its appearance, although, as was his wont, he had rehearsed the experiment just prior to the lecture. It happened that his assistant had handed to him a sample of the benzene which had been made in the lecture course by heating benzoic acid with lime, and at once drew his attention to the fact that the rehearsal had been made with the ordinary laboratory supply, which, of course, was derived from coal tar. It was soon definitely established that it was only coal-tar benzene that gave the indophenin reaction. Meyer's first idea was that it might be occasioned by an isomeric, a second benzene found in coal tar; but he quickly ascertained that the reaction was due to some sulphuretted product and that Baeyer's indophenin was a sulphur compound. He found that coal-tar benzene, after repeated shaking with oil of vitriol, no longer reacted with isatin, and it was among the sulphonic acids so formed that he discovered the reactive substance. This he was at first inclined to call *thianthren*, then *thiophan*, next *thiol*, and lastly *thiophen*, to denote that it was a sulphur-containing substance giving derivatives analogous to those of phenyl. Within about six months of his first observation, he was in a position to show to the Swiss Naturforscher Versammlung, by actual preparations, that its chemistry was hardly less extensive than that of benzene itself. In 1888 he published, in the form of a monograph—*Die Thiophengruppe* (Braunschweig: Vieweg u. Sohn)—an account of its condition at that time, from which it appears that, during the preceding five years, no fewer than 106 contributions to its history had been made from his own laboratory, and some 40 from those of others.

On the death of Hübner, Meyer received a call to Göttingen, which he accepted, and where a new laboratory was to be built for him. Here he continued his pyrochemical work, and his investigation of the thiophen derivatives, and began with Paul Jacobson the admirable *Text-book of Organic Chemistry*, which, in the critical selection and arrangement of its material, is unsurpassed. With Auwers, he resumed the study of benzil and its derivatives, which he had begun with Wittenberg and Goldschmidt, and with Münchmeyer he commenced the study of the behaviour of phenylhydrazine towards various groups of oxygen compounds. With Demuth, he undertook the investigation of the sulphuranes. Other notable papers of this period

were on isophthalaldehyde; on the negative nature of the phenyl group; on the thio-derivatives of deoxybenzoin and its analogues (desaurins); and with Riecke on the carbon atom and valency.

Stereochemical questions—we owe the phrase to Meyer—occupied much of his thought at this period. His perspicacity and insight are well illustrated in the lecture he gave to the German Chemical Society, in 1890, on the results and aims of stereochemical research. It is of interest to the student as giving a fairly complete historical account of the development of space formulæ, and more especially for the criticism of the work of Baeyer and Wislicenus on the stereochemical formulæ of single-, double-, and treble-linked carbon compounds, and of the stereochemical conceptions of Hantzsch and Werner in the case of nitrogen compounds. To this period belongs also his work on the aromatic nitriles, on tetramethylsuccinic acid, and on the oximes of phenanthraquinone.

Meyer was not destined to remain long in Göttingen. The new laboratory was barely finished when, in 1889, he received a call to Heidelberg, as successor to Bunsen. To Heidelberg accordingly he went with the coveted title of Geheimrath and the promise of a new and enlarged laboratory. Although only forty years of age, he was now, so far as worldly position was concerned, at the summit of his career. In conjunction with a number of his pupils he began the investigation of the conditions determining both the gradual and the explosive combustion of gaseous mixtures, notably of electrolytic gas, and of the simpler hydrocarbons with oxygen. In the case of mixtures of aliphatic hydrocarbons with equivalent amounts of oxygen, it appeared that the temperature of explosion falls as the number of the carbon atoms in the molecule increases; that it is probably lower for primary than for corresponding secondary hydrocarbons; and is less for hydrocarbons containing a double bond than for those containing only single bonds, and is still less for those containing a triple bond.

In 1892, Meyer and Wachter announced the existence of the iodoso-compounds, a series of aromatic derivatives in which the monovalent group IO replaces hydrogen. The study of these compounds led to the discovery of the remarkable substances known as the iodonium bases —compounds in which two of the valencies of the trivalent iodine atom are satisfied by aromatic radicles, while the third is satisfied in the free base by hydroxyl, and in the salts by an acid radicle. The iodonium bases are readily soluble in water, are strongly alkaline, and in their behaviour, as in that of their salts, show a remarkable similarity with the derivatives of silver, lead, and more particularly thallium.

Reference was also made to the study of the conditions determining the formation and hydrolysis of ethereal salts of aromatic acids which

occupied Meyer, in conjunction with his pupils, and more especially Sudborough, from 1894 up to the year of his death.

Meyer contributed to the literature of chemistry, either alone or in conjunction with his pupils, upwards of 300 memoirs and papers.

As the director of a large chemical laboratory, and as a laboratory teacher, Meyer worthily followed in the footsteps of Bunsen. He was an admirable lecturer, clear, vigorous, and extremely lucid, and his lectures were most popular. As a teacher, he had a wonderful faculty of infusing enthusiasm into his students. His literary ability, combined with his power of exposition, made him an admirable writer of popular science articles. His merits were recognised in every land where science is cultivated, and he was an Honorary Member of many Continental academies. The Royal Society awarded him the Davy Medal in 1891, and in the spring of that year he attended the celebration of the Jubilee of the Chemical Society, and the eloquent words which he uttered in responding to the toast of "Our Foreign Members" will not readily be forgotten by those who attended the banquet on that occasion.

On the motion of Professor DEWAR, seconded by Dr. ARMSTRONG, a vote of thanks was passed to the President for his lecture.

February 15th, 1900. Professor THORPE, F.R.S., President, in the Chair.

Messrs. J. Dewhirst, Edgar M. Chapman, and Thomas A. Henry were formally admitted Fellows of the Society.

It was announced that the following changes in the Council were proposed by the Council:—

As *Vice-Presidents*—Professor Divers, M.D., F.R.S., and Dr. T. Stevenson, *vice* Professor Ramsay, F.R.S., and Professor Emerson Reynolds, F.R.S.

As *Ordinary Members of Council*—Dr. Chattaway, Professor Collie, F.R.S., Professor Augustus Dixon, M.D., and Mr. W. J. Pope, *vice* Mr. Bevan, Dr. Moody, Dr. H. F. Morley, and Professor Smithells.

Certificates were read for the first time in favour of Messrs. Alexander William Bain, 2, Muswell Rise, Highgate, N.; Arthur Charles Davis, 3, Vinery Road, Cambridge; Noel Fielding Deerr, 26, South Parade, Chelsea, S.W.; Adolf Liebmann, 10, Marsden Street, Manchester; Frederick Thomas Munton, The Oak House, Winsford, Cheshire; James Wallace Sandford, Adelaide, S.A.; Bertram D. Steele, 40, Herndale Road, London, S.W.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—

Frederick Nolan Baker; Alexander Hutcheon Bennett; Sidney Calvert, M.A., B.Sc.; Oscar Joseph Cole, B.A.; William Francis Cooper, B.A.; Thomas Cuthbert Davison; Harry M. Dawson, B.Sc., Ph.D.; Stephen M. Dixon, B.A.; Alexander Findlay, M.A., B.Sc.; James Foulds; Granville Reginald Gee; Julius Geldard; Robert W. Gray; Alfred William Harvey; Herbert William Hart; Adam Houston; Henry William Hutchin; Henry Jackson, B.A., B.Sc.; Thomas Goode Joyce, B.Sc.; W. C. Robert Kynaston; Arthur Robert Laws; Thomas Ebenezer Mackenzie; Willam Mair; A. W. Cranbrook Menzies, M.A., B.Sc.; J. L. Rutgers Morgan, M.A., Ph.D.; Edgar Ford Morris, M.A.; Herbert Newall Morris; Ernest Brooks Naylor, B.Sc.; James Fraser Readman; Walter A. Riley; James McConnell Sanders; Fred Pilkington Sargeant; Edward Shrapnell Smith; James Hart-Smith; Bertram Vincent Storr, B.Sc.; Archie Hugh Strong; Gustavus A. Waterhouse, B.Sc.; Leonard Philip Wilson.

Messrs. A. W. Crossley, F. J. M. Page, and E. W. Voelcker were appointed to audit the Society's accounts.

Of the following papers, those marked * were read.

***17. "Ammonium amidosulphite." By Edward Divers and Masataka Ogawa.**

When dry enough, ammonia does not combine with sulphur dioxide at a low temperature. When less dry, it does so, with such rise of temperature that the product of the union is at once partly decomposed. But by dissolving the ammonia in dry, alcohol-free ether, and passing the sulphur dioxide into the solution, kept very cold, the product is precipitated undecomposed. It is colourless, very deliquescent, and unstable in the air. It dissolves in water with a hissing sound, and, when the water has been well cooled, yields a solution which gives the reactions of ammonium sulphite only. It is also very soluble in absolute alcohol, forming the salt lately described by the authors, ethyl ammoniumsulphite. It is formed from two mols. ammonia and one mol. sulphur dioxide. In a dry atmosphere, at temperatures such as 35°, it loses nearly half of its ammonia, as well as a little water. After the decomposition, no sulphite-forming substance remains, and the mass is somewhat orange-coloured from the presence of a very small quantity of a red substance. A very little sulphate is also present, but the residue consists mainly of substances the composition and nature of which are not yet fully determined. They seem to be thio-amido-sulphonic compounds, as yet unknown, which, by heat, by spontaneous partial hydration, or by treatment with ammonia in alcoholic solution, yield sulphur, sulphur dioxide,

sulphate, thiosulphate, amidosulphate, imidosulphate, and, almost certainly, sulphamide; when dissolved in water they give a reaction with silver nitrate, closely resembling, yet not that of a trithionate, for when acidified, their solution gives no sulphur or sulphur dioxide or only mere traces until it has been heated under pressure or for a long time.

The undecomposed salt appears to be correctly named *ammonium amidosulphite*, and to have the formula $NH_2 \cdot SO_2 \cdot NH_4$. The preparation of this salt shows Rose's assertion, that the gases unite only in equal volumes forming an orange substance which at once decomposes with water into sulphate and trithionate, to be altogether wrong and to be due to his having failed to prevent the decomposition of the product first formed.

***18. "On the products obtained by heating ammonium sulphites, thiosulphate, and trithionate." By Edward Divers and Masataka Ogawa.**

The authors have ascertained that *anhydrous ammonium sulphite* and *pyrosulphite* sublime unchanged at about 150° in a current of dry nitrogen, the vapours being no doubt the dissociated gases. At a temperature somewhat higher, *ammonium trithionate* decomposes into sulphur dioxide, sulphur, and ammonium sulphate. At about 150°, *ammonium thiosulphate* decomposes almost entirely, leaving a residue of sulphur and giving a sublimate of anhydrous ammonium sulphite; very small quantities of ammonia and hydrogen sulphide are also given off, giving rise possibly to a trace of trithionate. According to Spring, ammonium thiosulphate sublimes unchanged, except for temporary dissociation. To obtain the above results, moisture must be absent: the effect of slowly heating *hydrated ammonium sulphite* in a current of dry nitrogen is partly to dehydrate it, partly to convert it into pyrosulphite, at about 120°; and then at about 150°, the residue decomposes into sulphur dioxide and ammonium sulphite (approximately hemihydrated) which sublimes.

Ammonium trithionate, a very deliquescent and unstable salt, not hitherto described, was prepared from the potassium salt by the use of hydrofluosilicic acid and ammonia, being much too soluble to admit of preparation by Plessy's process for the potassium salt. *Ammonium sulphite* was conveniently precipitated by saturating its concentrated solution with ammonia in a cooling mixture, and the *pyrosulphite* by similarly saturating its solution with sulphur dioxide. *Anhydrous ammonium sulphite* was obtained by exposing the hydrated salt in a desiccator over potash in an ammoniacal atmosphere.

***19. "The colour of alkali nitrites." By Edward Divers.**

As Boguski (*J. Russ. Chem. Soc.*, 1899, **31**, 543) has published his observation that a solution of sodium nitrite had a slight yellow colour which he could not remove, and which he attributes to the presence of an impurity, the author wishes to recall attention to his own statement (*Trans.*, 1899, **75**, 86) that alkali nitrites have a slight yellow colour, especially in solution, and to Groves' statement in denial of its accuracy (*Proc.*, 1898, 14, 222). The author desires now to claim accuracy for his own statement. The colour of the potassium salt is much more manifest than that of the sodium salt, principally because of its ability to yield exceedingly concentrated solutions. Solutions of potassium nitrite, three parts of salt in one of water, are strongly yellow, particularly when thoroughly free from turbidity. Solutions of equal strength are equally coloured, whatever has been the source of the nitrite. Alkali nitrites are yellow in the fused state. The author is confident that Boguski's promised endeavour to remove the colour of sodium nitrite will be as futile as were those of chemists, long years ago, to remove the pink colour from manganous salts. Boguski's observation that the solid nitrite is sometimes apparently without colour, depends upon the well known optical effect of fine division in lessening the colour of transparent solids.

***20. "Solubility of mixed potassium nitrite and nitrate." By Edward Divers.**

By crystallising out, as far as possible, the nitrate which is mixed with potassium nitrite in its usual method of preparation, there remains a mixture of about three parts of nitrite to one part of nitrate, and this constitutes the ordinary nitrite of commerce. This mixture is soluble in one-fourth its weight of water, although the pure nitrite requires one-third of its weight, and the pure nitrate about four times its weight of water to dissolve it. Accordingly, when a solution of three parts pure potassium nitrite in one part water is digested with powdered potassium nitrate at the common temperature, it readily dissolves up one part of this salt.

Discussion.

In reply to remarks by Messrs. Baker, W. P. Bloxam, and Scott, Dr. Divers said that the ammonium amidosulphite rapidly deliquesced in air, and he quite agreed with Mr. Bloxam's observation as to the great activity of hydrated ammonium sulphite with regard to atmo-

spheric oxygen. As Rose had taken no precautions to maintain a low temperature during the reaction, there was no doubt that the compound resulting from the combination of two volumes of ammonia with one of sulphur dioxide gave off half of its ammonia again under the influence of the high temperature produced in the reaction.

***21. "The combination of sulphur dioxide with oxygen." By Edward John Russell and Norman Smith.**

The authors have found that when a mixture of sulphur dioxide and oxygen acts on certain oxides, in addition to the absorption of the sulphur dioxide, part of the sulphur dioxide and oxygen combine forming sulphur trioxide, this being apparently due to the "surface action" of the oxide. The extent of this "surface action" varies with the nature and physical conditions of each oxide. No sulphur trioxide was ever found unless a simultaneous absorption of sulphur dioxide occurred; when manganese peroxide and sulphur dioxide, dried by phosphorus pentoxide, were brought together, no absorption took place, nor was any sulphur trioxide produced on the addition of dried oxygen.

If a mixture of dried sulphur dioxide and oxygen be passed over well-dried platinised pumice heated to 400—450°, very little sulphur trioxide is formed, and the drier the materials the less is the combination.

***22. "Notes on the estimation of gaseous compounds of sulphur." By Edward John Russell.**

In this paper, volumetric methods of analysis are given which have been found to work satisfactorily in the estimation of sulphur dioxide, hydrogen sulphide, carbonyl sulphide, and carbon disulphide in gaseous mixtures. It is found that, except in the case of sulphur dioxide, absorption methods are not reliable; as a rule, by far the most satisfactory method is to explode with oxygen. In this explosion, sulphur dioxide and sulphur trioxide are both produced, the amount of the former being determined directly, and that of the latter calculated from the contraction observed after explosion. Sulphur dioxide is best estimated by absorption with a pellet of lead peroxide, since this substance, if freshly washed and not too dry, exerts but little of the surface action which tends to cause some of the sulphur dioxide to combine with part of the oxygen to form sulphur trioxide.

*23. "The influence of the 'nascent state' on the combination of dry carbon monoxide and oxygen." By Edward John Russell.

The author has studied several reactions in which carbon monoxide and excess of oxygen were brought together in the flame of an explosion, one or both being in the nascent condition. Combustion was rarely complete, and the amounts of carbon monoxide left unburnt were found to be very similar to those left unburnt in Dixon's experiments (*Trans.*, 1896, 784), in which dried mixtures of carbon monoxide and oxygen were fired by adding carbon disulphide and oxygen and sparking, although in the present experiments one of the substances (carbon monoxide) was in the nascent condition, whilst in Dixon's experiments it was not. It seems, therefore, that the nascent condition has no great effect in promoting combination between carbon monoxide and oxygen, although the high temperature produced by a violent reaction has a very considerable effect.

The substances used as sources of nascent carbon monoxide were carbonyl sulphide and nickel carbonyl; and for nascent oxygen, chlorine monoxide and chlorine peroxide.

It was discovered incidentally that mixtures of pure carbonyl sulphide and excess of oxygen are not exploded by an electric spark. If, however, a slight amount only of impurity is present an explosion takes place, but combustion is not complete, carbonyl sulphide remaining unburnt in large quantity, along with carbon monoxide, produced by the decomposition of some of the carbonyl sulphide. If the impurity is greater, the combustion is complete.

*24. "Asymmetric optically active tin compounds. Dextromethylethyl-*n*-propyl tin iodide. Preliminary note. By William Jackson Pope and Stanley John Peachey.

Hitherto no substance containing an atom of tin attached to four different groups has been obtained, owing to the lack of general methods for their preparation.

The authors find that compounds of the type $SnX^{I}X^{II}X^{III}X^{IV}$ can be readily prepared by aid of the following series of reactions from the trimethyl tin iodide described by Ladenburg and Cahours:

(1) $2Sn(CH_3)_3I + Zn(C_2H_5)_2 = 2Sn(CH_3)_3(C_2H_5) + ZnI_2$.

(2) $Sn(CH_3)_3(C_2H_5) + I_2 = Sn(CH_3)_2(C_2H_5)I + CH_3I$.

(3) $2Sn(CH_3)_2(C_2H_5)I + Zn(C_3H_7)_2 = 2Sn(CH_3)_2(C_2H_5)(C_3H_7) + ZnI_2$.

(4) $Sn(CH_3)_2(C_2H_5)(C_3H_7) + I_2 = Sn(CH_3)(C_2H_5)(C_3H_7)I + CH_3I$.

Externally compensated *methylethyl-*n*-propyl tin iodide*, $\begin{matrix}CH_3\\C_2H_5\end{matrix}\!\!>\!Sn\!<\!\begin{matrix}C_3H_7\\I\end{matrix}$,

the final product of reaction (4), is a faintly yellow oil boiling at 270° without decomposition; it is almost insoluble in water, and its vapour exercises unpleasant effects on the mucous membrane.

On agitating the iodide with a warm aqueous solution of a molecular proportion of silver dextrocamphorsulphonate and evaporating the filtered liquid, a copious deposit of *dextromethylethyl-n-propyl tin dextrocamphorsulphonate*, $Sn(CH_3)(C_2H_5)(C_3H_7)(C_{10}H_{15}OSO_3)$, was obtained; the salt is only sparingly soluble in cold water, and crystallises in lustrous, square plates melting at 125—126°. In dilute aqueous solution, it has the molecular rotation $[M]_D = +95°$, so that for the monobasic radicle, $\begin{matrix} CH_3 \\ C_2H_5 \\ C_3H_7 \end{matrix}\!\!>\!\!Sn-$, $[M]_D$ is about $+45°$.

On evaporating the mother liquor from which this salt had separated, further deposits of the same salt were obtained until all the water had been expelled, and the authors have been unable to isolate a salt of the lævo-base; this behaviour seems due to the conversion of the lævo-base into the dextro-base by continued racemisation in the following manner. The solution of externally compensated base with dextrocamphorsulphonic acid deposits a portion of its dextro-base as the sparingly soluble salt; the excess of lævo- over dextro-base remaining in the solution racemises as evaporation proceeds, a further portion of dextro-base separates as salt, and racemisation of the residue again proceeds. This case is the first of the kind recorded, and affords powerful support to Le Bel's hypothesis respecting the mobility of alkyl groups of low molecular weight in quaternary ammonium salts.

On treating the freshly prepared cold aqueous solution of the dextrocamphorsulphonate with potassium iodide solution, *dextromethylethyl-n-propyl tin iodide* separates as a faintly yellow oil; the highest specific rotation of the iodide which has yet been observed is $[\alpha]_D = +23°$ in ethereal solution. The rotation was, however, very variable, and, under conditions not yet understood, the separated iodide was optically inactive. This behaviour is due to racemisation.

It should be noted that the discovery noted above, that racemisation, due to intramolecular mobility, may cause rapid and complete conversion of an externally compensated base into one optically active isomeride, reopens the question of the space configuration of quadrivalent sulphur compounds which, in the light of previous knowledge, seemed to have been determined by our former results (*Proc.*, 1900, 16, 12).

Having now shown that quadrivalent asymmetric tin compounds can exist in enantiomorphously related configurations possessing optical activity, it follows that the space configuration of quadrivalent tin compounds is of the tetrahedral type already established for carbon

compounds, and substances of the type of tin tetrachloride must now be regarded as true atomic compounds. Having proved that asymmetric pentavalent nitrogen compounds (*Trans.*, 1899, **75**, 1127) also give rise to optical activity in the same way that van't Hoff and Le Bel proved it for carbon, it may be concluded that all enantiomorphous compounds must be optically active.

In Group IV of the periodic table the non-metal, carbon, is at the top, whilst the metal, tin, is near the bottom; since both can give rise to optical activity in their asymmetric compounds, it is highly probable that all the elements in Group IV lying between these are capable of acting as centres of optical activity. Should this hold for the whole of Group IV, and as it has been shown to hold for nitrogen, the first member of Group V, all the elements of the latter group may be expected to act as optically active centres in appropriate compounds. Compounds of the types $RX^{I}X^{II}X^{III}X^{IV}$ and $QX^{I}X^{II}X^{III}X^{IV}X^{V}$ should therefore be optically active, R being an atom of any element in Group IV, and Q an atom of any element in Group V.

The application of the reactions now described to other elements is in progress, and the authors hope shortly to communicate results obtained with quadrivalent lead compounds.

25. "Note on the refraction and magnetic rotation of hexamethylene." By Sydney Young, D.Sc., F.R.S., and Emily C. Fortey, B.Sc.

The specimen of hexamethylene obtained by one of the authors from Galician petroleum was found to contain a small quantity of a heptane. The hexamethylene was freed from the paraffin by fractional crystallisation, and its refraction and magnetic rotation were determined by Dr. W. H. Perkin, sen. The results obtained are given in the paper.

26. "Apiin and apigenin. Part II. Note on vitexin." By A. G. Perkin.

By the action of nitric acid on apigenin under varied conditions, four nitro-derivatives have been obtained: *mononitro-apigenin*, $C_{15}H_9O_5(NO)_2$, orange-yellow needles, m. p. about 302°, somewhat soluble in alcohol; *trinitro-apigenin* (*a*), $C_{15}H_7O_5(NO_2)_3$, yellow needles, m. p. about 296°; *trinitro-apigenin* (*b*), yellow needles, m. p. 245—246°, and *tetranitro-apigenin*, $C_{15}H_6O_5(NO_2)_4$, almost colourless needles, m. p. 243—244°. With the exception of the first mentioned, all dissolve with difficulty in the usual solvents. In preparing the mononitro-compound, *dinitro*-p-*hydroxybenzoic acid* was obtained as a decomposition product, a further proof that apigenin does not contain a

catechol group (*Trans.*, 1897, **71**, 805). Tetranitro-apigenin appears to be identical with the compound, $C_{15}H_6O_5(NO_2)_4$, obtained from vitexin (*Trans.*, 1898, **73**, 1026), and as the decomposition products of both colouring matters are identical, vitexin must be a derivative of apigenin. The formulæ $C_{21}H_{20}O_{10}$ and $C_{21}H_{13}O_{10}(C_2H_3O)_7$ are now assigned to vitexin and acetylvitexin, and it is suggested that vitexin is *a stable glucoside of apigenin*, and that a like constitution may also apply to scoparin (*Proc.*, 1899, **15**, 123), which, according to this view, is a glucoside of a luteolin monomethyl ether.

Apiin, $C_{27}H_{32}O_{16}$, the glucoside of apigenin occurring in *Apium petroselinum*, is not converted by dilute nitric acid into nitro-apigenin, but into *nitro-apigetrin*, $C_{21}H_{21}O_{11}NO_2$, a yellow, crystalline powder very sparingly soluble in the usual solvents. This is the nitro-compound of a new glucoside, apigetrin, which differs from apigenin in containing but one sugar group. By prolonged digestion with dilute hydrochloric acid, it yields the above mononitro-apigenin.

27. "The yellow colouring principles of various tannin matters. VII." By A. G. Perkin.

The colouring matter of the leaves of *Arctostaphylos uva-ursi* (bear-berry) and *Hæmatoxylon Campeachianum* (logwood) is *quercetin*, and this is accompanied by a second substance, probably *myricetin*, to which the green colour of its alkaline solutions are due. *Gallotannic acid* occurs in some quantity in the latter leaves. The leaves of *Rhus metopium* contain *gallotannin*, *myricetin*, and a trace of *quercetin*, but the stem of this plant, unlike *R. cotinus*, and *R. rhodanthema* is devoid of colouring matter. The sparing solubilities of acetylmyricetin and dibromoquercetin have been employed for the separation of myricetin and quercetin. The leaves of *Robinia pseudacacia* contain a feeble colouring matter, *acacetin*, $C_{16}H_{12}O_5$, which yields an *acetyl* derivative, $C_{16}H_{10}O_5(C_2H_3O)_2$, colourless needles, m. p. 195—198°, and on fusion with alkali *phloroglucinol*, *p-hydroxybenzoic acid*, and a trace of *protocatechuic acid*. Acacetin contains one methoxyl group, on removal of which a colouring matter, $C_{15}H_{10}O_5$, results, having the reactions of apigenin. It is thus probably an *apigenin monomethyl ether*. The leaves of *Myrica gale* and *Coriaria myrtifolia* contain respectively *myricetin* and *quercetin*. Although a relationship frequently exists between the tanning and the colouring matters of the same plant (*Trans.*, 1897, **71**, 1138), there is no rule on this point, for exceptions are somewhat numerous.

28. "Note on the bromo-derivatives of camphopyric acid." By J. Addyman Gardner.

An atom of hydrogen in camphopyric acid may be readily replaced by bromine, by the action of the halogen in the presence of phosphorus. Two acids of the formula $C_9H_{13}BrO_4$, are thus obtained and are provisionally named α- and β-bromocamphopyric acid. These acids may be prepared either by treating camphopyric acid with phosphorus pentachloride and subsequently warming with bromine, or by mixing the acid with amorphous phosphorus and adding the proper amount of bromine. In either case, the product is poured into cold water, when part of the acid separates in the solid state and part is extracted with ether from the solution. The α- and β-acids may be separated by repeated crystallisation from benzene.

If only a small amount of water is used to decompose the acid bromides, bromocamphopyric anhydride is also obtained.

α-Bromocamphopyric acid separates from benzene or chloroform as a very light, white, crystalline powder, melting at 167° with previous softening. It is very moderately soluble in hot benzene and chloroform, but only slightly in cold; it is also very soluble in water, ether, acetone and ethyl acetate. It is a dibasic acid, and forms very soluble sodium, barium and ammonium salts.

α-Bromocamphopyric anhydride, $C_9H_{11}BrO_3$, may be obtained by treating the acid in the usual way with acetyl chloride or acetic anhydride. It crystallises readily from benzene in well-defined, tabular crystals which melt at 226—227°. These crystals are very soluble in ether, acetone and ethyl acetate.

β-Bromocamphopyric acid is more soluble in benzene than its isomeride, and is obtained, though in very small quantity, from the mother liquors of the α-acid. It is a white, crystalline substance melting at 207—208°, quite different in appearance from its isomeride. Its barium salt is soluble, and has the formula $Ba(C_9H_{12}BrO_4)_2,4H_2O$; this acid has not, however, been obtained in sufficient quantity for a more complete investigation.

The same products are obtained when camphoic acid is similarly treated with phosphorus pentachloride and bromine.

α-Hydroxycamphopyric acid, $C_9H_{13}(OH)O_4$. If α-bromocamphopyric acid is heated for some time with a 10 per cent. solution of potash, then acidified with hydrochloric acid and extracted with ether, an oily acid is obtained which for the most part solidifies on standing. If this be boiled with benzene, the oily portion dissolves, and a white solid is left which, on crystallisation from water, may be obtained in well-defined, colourless, transparent crystals which melt at 206—207°.

This substance is a dibasic acid and has the formula $C_9H_{14}O_5$. Its sodium and barium salts, which are very soluble in water, were analysed. It is only very slightly soluble in benzene, chloroform, and carbon bisulphide, but dissolves easily in ethyl acetate and in hot water; the oil obtained along with it is apparently an unsaturated acid, but has not yet been obtained in a state of sufficient purity for investigation. These substances are being prepared in quantity, and the author hopes before long to be able to bring before the Society a more complete account of their properties and reactions.

ADDITIONS TO THE LIBRARY.

I. Donation.

Luff, A. P., and Page, F. J. M. A manual of chemistry, inorganic and organic, with an introduction to the study of chemistry. Ill. London 1900. From the Authors.

II. By Purchase.

Gessmann, G. W. Die Geheimsymbole der Chemie und Medicin des Mittelalters. Ill. Graz 1899.

Pamphlet.

Clowes, Frank, and Houston, A. C. Bacterial treatment of crude sewage (supplement to second report). Note on the deposit which accumulates on the coke fragments of the coke-beds at Barking and Crossness. From the Authors.

At the next meeting on Thursday, March 1st, at 8 p.m., the following papers will be communicated:—

"Pilocarpine and the alkaloids of Jaborandi leaves." By H. A. D. Jowett, D.Sc.

"Isomeric partially racemic salts containing pentavalent nitrogen." Parts I to VII. By F. S. Kipping, D.Sc., F.R.S.

"New synthesis of indene." By F. S. Kipping, D.Sc., F.R.S., and Harold Hall.

"Potassium nitrito-hydroximidosulphates and the non-existence of dihydroxylamine derivatives." By E. Divers, D.Sc., F.R.S., and T. Haga, D.Sc.

"Identification and constitution of Fremy's sulphazotised salts of potassium." By E. Divers, D.Sc., F.R.S., and T. Haga, D.Sc.

"Some acids obtained from α-dibromocamphor." By A. Lapworth, D.Sc., and E. M. Chapman.

"Campholytic and isolauronolic acids." By J. Walker and W. Cormack.

"The configuration of the camphoric acids." By J. Walker and J. K. Wood.

"The constitution of camphoric acid." By J. Walker.

An extra Meeting of the Society will be held on Thursday, March 8th, when a lecture on "**Recent Researches on Nitrification**" will be given by Professor Warington, F.R.S. The Chair will be taken at 8.30 p.m.

RICHARD CLAY AND SONS, LIMITED, LONDON AND BUNGAY.

Issued 7/3/1900.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 16. **No. 220.**

March 1st, 1900. Professor THORPE, F.R.S., President, in the Chair.

Mr. J. W. Anderson was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Henry Jennings, Marlowes, Hemel Hempstead, Herts; Robert Pettigrew, 50, Cresswell Grove, West Didsbury, Manchester; Geoffrey Surtees Phillpotts, 82, James's Street, Dublin.

Of the following papers, those marked * were read:—

***29. "On pilocarpine and the alkaloids of jaborandi leaves." By H. A. D. Jowett, D.Sc.**

On account of the doubts expressed by Kundsen, Merck, and others as to the reliability of the work of Hardy and Calmels on this subject, and the recent conflicting statements of Petit and Polonowsky and of Merck, the author has undertaken a complete study of these alkaloids. The present paper deals with the characterisation of pilocarpine, isopilocarpine (pilocarpidine of Petit and Polonowsky), pilocarpidine and jaborine, with a few preliminary experiments on the constitution of the alkaloid. The results, which are given in detail in the paper, may be briefly summarised as follows:

1. The original papers of Hardy and Calmels are very unsatisfactory, as they contain neither physical constants nor analyses of the products described. In most cases, the author is unable to confirm their results. On the other hand, a satisfactory explanation is afforded of the apparent contradiction between the work of Petit and Polonowsky and that of Merck.

2. The physical constants and description of the salts of pilocarpine, as given by Petit and Polonowsky, are generally confirmed, though in several cases there are slight differences, due probably to the use of purer material by the author.

3. The acid character of pilocarpine has been investigated and the previous work of Hardy and Calmels on this subject corrected.

4. The existence of a base, isomeric with pilocarpine, and produced from it by the action of heat or alkali, as previously stated by Petit and Polonowsky, is confirmed. As this base is isomeric with and bears a close relation to pilocarpine, it is proposed to call it isopilocarpine, as the term pilocarpidine, previously used for it, must be retained for the product previously described by Harnack under this name. It is shown that isopilocarpine can be distilled unchanged in a vaccuum.

5. Some of the physical constants of isopilocarpine and its salts as given by Petit and Polonowsky are confirmed, and others corrected.

6. Proof is given of the existence of isopilocarpine in jaborandi leaves and in the pilocarpine nitrate of commerce.

7. The existence of the pilocarpidine of Harnack and Merck and their statements regarding its composition are confirmed. Some of the salts of the base are described.

8. The absence of pilocarpidine in the pilocarpine nitrate of commerce and in the varieties of jaborandi leaves at present in the market is proved.

9. The jaborine of commerce is shown to be a mixture of isopilocarpine, pilocarpidine, and a trace of pilocarpine with colouring matter. No evidence has been obtained of the existence of an alkaloid with the properties of jaborine, or of any other than those described in this paper.

10. Several experiments on the constitution of pilocarpine have been repeated, and the results of Hardy and Calmels corrected.

Further experiments on this subject are in progress.

The author has been unable to obtain any evidence confirmatory of the constitutional formula which was proposed by Hardy and Calmels and widely adopted.

Discussion.

Mr. Kingzett referred to his work on pilocarpine, which was communicated to the Society in 1876. He then proposed for this alkaloid the formula $C_{23}H_{35}N_4O_4$, and although this formula had been modified by later workers to $C_{11}H_{16}N_2O_2$, which was also adopted by Dr. Jowett, he still adhered to the formula he had originally suggested, because it was based on several concordant analytical results.

Professor Dunstan said that our knowledge of the chemistry of

pilocarpine and the alkaloids of jaborandi was in a very uncertain state, and he was glad to find that Dr. Jowett had commenced its careful revision. The alleged existence of jaborine, an alkaloid antagonistic to pilocarpine, had long been a difficulty in the medicinal employment of this drug. Dr. Jowett appeared to have shown good grounds for the conclusion that no such alkaloid as jaborine exists in the plant, and he had made a serious criticism of the generally accepted results and conclusions of Hardy and Calmels.

***30. "Isomeric partially racemic salts containing quinquevalent nitrogen."**

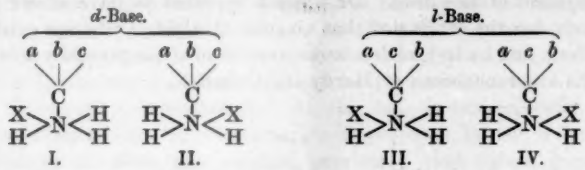
Hydrindamine bromocamphorsulphonates, chlorocamphorsulphonates and *cis*-π-camphanates. By F. Stanley Kipping, Ph.D., D.Sc., F.R.S.

On continuing the investigation of the isomeric hydrindamine bromocamphorsulphonates already briefly described (*Proc.*, 1899, **15**, 172), it has been found that both compounds, when decomposed by barium hydroxide, yield a base identical with externally compensated hydrindamine. It is proved that the optical inactivity of the base is not due to racemisation having occurred, hence the formation of the two bromocamphorsulphonates cannot be attributed to a resolution of the base into its enantiomorphous components. As to the possibility of the existence of two isomeric forms of bromocamphorsulphonic acid, it is shown that the acid in each salt is the same. Hence it is concluded that the isomeric hydrindamine bromocamphorsulphonates are both partially racemic salts.

The specific rotations of these salts are different in alcoholic solutions of equal concentration; their specific rotations in 1 per cent. aqueous solutions are, for the more sparingly soluble α-salt $[\alpha]_D = +60°$, and for the β-salt $[\alpha]_D = +49{\cdot}7°$, hence the molecular rotations are $[M]_D = +266{\cdot}5°$ and $[M]_D = +220{\cdot}5°$ respectively. As the molecular rotation of bromocamphorsulphonic acid, calculated from the determinations of Walden (*Zeit. phys. Chem.*, 1894, **15**, 196) and from data given in the paper is +270°, the low molecular rotation of the β-salt might be taken to indicate either the existence of an isomeric form of bromocamphorsulphonic acid or the presence of lævorotatory hydrindamine. It is shown that as the salt in question is composed of *d*-hydrindamine α-bromocamphorsulphonate and *l*-hydrindamine α-bromocamphorsulphonate, which salts have probably widely different specific rotations in a non-dissociated condition, the apparently abnormal molecular rotation of the β-salt may be attributed to incomplete ionic dissociation.

The following is the explanation of this form of isomerism suggested

by the author; it is equally applicable to all the other cases of isomerism of this kind which he has observed. When an externally compensated base combines with an optically active acid, four different salts may be produced, as the following formulæ indicate:



Of these four compounds, no two are mirror images, but as the relation between I and IV, on the one hand, and II and III, on the other, would probably be that of mirror images if the group X were not enantiomorphous, it may be presumed that I and IV would be formed in equal quantities, and might unite to form a partially racemic salt; the isomeric partially racemic salt would be similarly produced from II and III.

Externally-compensated hydrindamine unites with chlorocamphorsulphonic acid to form unequal quantities of two salts which are isomeric when anhydrous, but which are usually differently hydrated. The more sparingly soluble α-salt, which is produced in by far the larger quantity, crystallises from water in opaque, very slender prisms, whereas the β-isomeride is usually deposited in more transparent and compact prisms.

The relationship between these two salts is analogous to that of the compounds above described, but the β-salt differs from the corresponding salt of the bromo-acid, as it exists in two differently hydrated forms, one of which is indistinguishable in appearance from the α-salt. The conditions which determine the formation of one or other variety of the β-salt are not yet known with certainty.

The α- and β-compounds are both partially racemic salts which are not convertible the one into the other by ordinary solvents, but by repeatedly evaporating a solution of the β-salt with externally-compensated hydrindamine, the α-isomeride is obtained.

The specific rotations of the isomerides in alcoholic solution are practically identical, but when dissolved in water, and especially in chloroform, different values are obtained. Determinations in approximately 1 per cent. aqueous solutions gave the following average results: for the α-salt $[\alpha]_D = +47°$, $[M]_D = +188°$; for the β-salt $[\alpha = +50{\cdot}5°$, $[M]_D = +202°$.

The molecular rotation of chlorocamphorsulphonic acid was found to be $[M]_D = +189°$, so that the molecular rotations of the partially racemic salts are practically identical with the values they might be

expected to give under the above conditions. The two differently hydrated forms of the β-salt were found to have the same specific rotation when calculated for the anhydrous salt.

When externally-compensated hydrindamine is neutralised with *cis*-π-camphanic acid, unequal quantities of two isomeric anhydrous salts are obtained. The more sparingly soluble α-compound melts at about 192°, the isomeric β-salt at about 172°; when crystallised from water or other solvents, both salts are deposited in very slender prisms practically identical in appearance. The base liberated from either of these salts by barium hydroxide is optically inactive, and as each salt, when directly decomposed by strong hydrochloric acid, gives optically inactive hydrindamine hydrochloride, it is clear that the two salts do not correspond with the two enantiomorphous hydrindamines, but that both are partially racemic substances.

The β-salt may be converted into the α-form by evaporating its aqueous solution with externally compensated hydrindamine, which seems to indicate that the relation between these two salts is similar to that between the isomeric salts of chloro- and bromo-camphorsulphonic acids from which they differ in undergoing hydrolytic dissociation, and this leads to other differences in behaviour, such as the conversion of the one salt into the other in aqueous, and apparently also in alcoholic solution, rendering their separation and the determination of their properties a matter of some difficulty.

Determinations of the specific rotations of these salts in solution in methyl alcohol showed wide variations; different preparations of the α-salt, all melting at the same temperature, gave values for $[\alpha]_D$ varying from $-2°$ to $+20°$, and in the case of β-salt from $-6°$ to $-10°$. By repeated fractional crystallisation, these values were considerably raised, the greatest rotation for the α-salt being $[\alpha]_D = +24°$, and for the β-salt $[\alpha]_D = -20°$.

In solution in methyl alcohol, the rotation of the α-salt is very low at first, being $[\alpha]_D = +5°$ a few minutes after solution; after 45 minutes, it rises to $[\alpha]_D = 24°$, at which it seems to remain constant. The cause of this change is not clear, as the β-salt, in other respects so similar, does not show it. In dilute aqueous solutions, both salts have practically the same rotation, $[\alpha]_D = -16°$, and the molecular rotation calculated from determinations in 1 per cent. aqueous solutions is $[M]_D = -53°$ approximately, a value agreeing fairly well with that obtained for *cis*-π-camphanic acid from an examination of its piperidine salt and of its solution in dilute aqueous ammonia.

***31. "New syntheses of indene." By F. Stanley Kipping, Ph.D., D.Sc., F.R.S., and Harold Hall, A.I.C.**

In the course of some work connected with α-hydrindamine, it was found that the hydrochloride of this base is readily decomposed when heated, giving a distillate of indene, and a residue of ammonium chloride, $C_6H_4<\begin{matrix}CH_2\\CH\\|\\NH_2,HCl\end{matrix}>CH_2 = C_6H_4<\begin{matrix}CH_2\\CH\end{matrix}>CH + NH_4Cl$; the reaction seems to take place almost quantitatively, and affords the most convenient method yet known for the preparation of this unsaturated hydrocarbon. Trimethylhydrindamine iodide undergoes a similar decomposition when it is heated, yielding indene and trimethylamine hydriodide. The indene obtained by either of these methods is identical with the hydrocarbon isolated from coal-tar by Krämer and Spilker, and also with that obtained by Perkin and Revay by the distillation of hydrindenecarboxylic acid (*Trans.*, 1894, **66**, 228). The identity of all three preparations was established, the differences between synthetical and coal-tar indene observed by Perkin and Revay (*loc. cit.*) being doubtless due to the presence in the latter of impurities which they were unable to remove.

Trimethylhydrindamine iodide, $C_9H_9N(CH_3)_3I$, is obtained when hydrindamine is treated with methyl iodide at ordinary temperatures; it crystallises well, is dimorphous, and melts at about 190°.

It seems probable that the reactions described above will also occur in the case of the hydrochlorides of other aromatic partially reduced bases, and experiments will be made to test this.

***32. "Potassium nitrito-hydroximidosulphates and the non-existence of dihydroxylamine derivatives." By E. Divers and T. Haga.**

Potassium nitrite forms crystalline compounds with the normal, the 2/3 normal, and the 5/6 normal potassium hydroximidosulphates, all readily decomposed by solution in water, but recrystallisable from sufficiently concentrated solutions of potassium nitrite or of this salt and some potassium hydroxide. Their formulæ are $KNO_2,2K_3NS_2O_7,4OH_2$;

$KNO_2,K_2HNS_2O_7$; $7KNO_2,2K_5H(NS_2O_7)_2,3OH_2$;

$3KNO_2,K_5H(NS_2O_7)_2,OH_2$; $7KNO_2,3K_5H(NS_2O_7)_2$.

The discovery of these salts has enabled the authors to destroy what little evidence there was for the existence of *dihydroxylamine* compounds, two of which have been described by Raschig. One of these he treats as being dipotassium monosulphonated dihydroxyl-

amine, $\begin{matrix}HO\\KO\end{matrix}\!\!>\!NSO_3K$, and the other, more easily obtained, as the anhydro-compound of this with potassium monosulphonated dihydroxylamine,' $\begin{matrix}HO\\KSO_3\end{matrix}\!\!>\!NON<\!\!\begin{matrix}OK\\SO_3K\end{matrix}$. The authors have followed Raschig's methods pretty closely and with a sufficient degree of success, and have found his preparations indistinguishable from synthetically prepared compounds, somewhat impure, of nitrite with the 5/6 normal hydroximidosulphate, and the 2/3 normal hydroximidosulphate respectively. According to them, the anhydro-'dihydroxylamine' compound was $KNO_2,K_2HNS_2O_7$, whilst the other was impure $3KNO_2,K_5H(NS_2O_7)_2,OH_2$. Two other salts prepared by Raschig, which have figured respectively as an isomeride of Pelouze's hyponitrososulphate and as an isomeride of the 5/6 normal hydroximidosulphate, are considered by the authors to be also only impure nitritohydroximidosulphates.

***33. "Identification and constitution of Fremy's 'sulphazotised salts of potassium.'" By E. Divers and T. Haga.**

By treating a solution of potassium nitrite and hydroxide with sulphur dioxide, Fremy in 1845 obtained a series of salts, and by their hydrolysis or oxidation, other salts, all sulphonated derivatives of nitrous acid. The constitution of several of these has remained undetermined; attempts to reproduce some of them have failed to such an extent as to make even their existence doubtful. The authors have been fairly successful in obtaining Fremy's results, and with the help of the knowledge summarised in the preceding abstract, are able to express the constitution of his salts with confidence. His *sulphazate*, which neither Claus nor Raschig succeeded in obtaining, was made without difficulty by following Fremy's directions. It is the potassium nitrito-2/3-normal hydroximidosulphate partly converted, by treatment with alkali, into the normal hydroximidosulphate. His *sulphazite* is the nitrito-5/6-normal hydroximidosulphate of which the formula is given in the preceding abstract. His *metasulphazate* is described as a jelly, which on pressure in a cloth became wax-like. The authors have obtained a salt in fine, silky fibres in all other respects apparently identical with that of Fremy, and this proved to be potassium nitrito-normal hydroximidosulphate, mixed with a little normal hydroximidosulphate. His *metasulphazotate*, as obtained by the authors, proved to be the potassium nitrito-2/3-normal hydroximidosulphate, mixed or combined with a little normal hydroximidosulphate. The constitution of Fremy's *basic* and *neutral sulph-*

azotates, sulphazidate, sulphammonate, and *sulphamidate* have been already determined, whilst his *sulvhazilate* and *metasulphazilate* appear to have the formulæ $ON:(SO_3K)_2$ and $ON:(SO_3K)_3$.

***34. "Some acids obtained from α-dibromocamphor." By Arthur Lapworth and Edgar M. Chapman.**

Camphonic acid is the name the authors propose for the acid obtained by hydrolysing α-monobromocampholid (compare Forster, *Trans.*, 1896, **69**, 51). It has the formula $C_{10}H_{16}O_3$, crystallises from ethyl acetate in prisms melting at 194°, and appears to be dimorphous. It has all the properties of a ketonic acid, a fact which shows conclusively that α-monobromocampholid contains the group $-\underset{|}{C}Br\cdots\cdots CO\cdot\underset{|}{O}$. The *oxime*, $CO_2H\cdot C_9H_{15}:N\cdot OH$, forms slender needles melting at 125—127°; the *semicarbazone*, $CO_2H\cdot C_9H_{15}:N_2H\cdot CO\cdot NH_2$, crystallises in flattened needles which melt and decompose at 222—223°. The *phenylhydrazone* and p-*bromophenylhydrazone* were obtained as colourless, pulverulent substances, which yielded well-characterised sodium salts.

Dibromocamphonic acid, $C_9H_{13}OBr_2\cdot CO_2H$, is obtained on adding bromine to a solution of camphonic acid in chloroform; it melts and decomposes at 144°. *Monobromocamphonolactone*, $C_{\underset{|}{9}}H_{12}OBr\cdot CO\cdot\underset{|}{O}$, is formed when the sodium salt of the dibromo-acid is boiled with water; it crystallises in glistening needles or prisms melting at 110—111°. *Tribromocamphonolactone*, $C_{\underset{|}{9}}H_{11}OBr_2\cdot CO\cdot\underset{|}{O}$, produced by gently warming dibromocamphonic acid with excess of bromine, melts at 166—167°.

The formation of a tribromolactone from camphonic acid, taken in conjunction with the rest of the evidence relating to the derivatives of camphorenic acid, shows, with some degree of probability, that bromocamphorenic acid has the formula $CH\begin{matrix}<\\>\end{matrix}\begin{matrix}CH_2\cdot CMe_2\\CBr—CH_2\end{matrix}\begin{matrix}>\\\end{matrix}CMe\cdot CO_2H$, and not $CH\begin{matrix}<\\>\end{matrix}\begin{matrix}CBr\cdot CMe_2\\CH_2—CH_2\end{matrix}\begin{matrix}>\\\end{matrix}CMe\cdot CO_2H$, for which a preference has been expressed by one of the authors (*Trans.*, 1899, **75**, 1139).

Camphonic acid unites with hydrocyanic acid, and on treating the product with hydrochloric acid, two new *acids*, $C_{\underset{|}{9}}H_{15}\begin{matrix}<\\\end{matrix}\begin{matrix}CO_2H\\CO\cdot\underset{|}{O}\end{matrix}$ and $C_9H_{15}(OH)\begin{matrix}<\\\end{matrix}\begin{matrix}CO_2H\\CO_2H\end{matrix}$, are obtained. The former crystallises in long needles melting at 144—145°, the latter forms orthorhombic plates melting, with formation of an anhydride, at 207°, and cannot be obtained by hydrolysing the lactonic acid.

Homocamphoronic acid is rapidly attacked by bromine at 140°, but

the product is nearly free from bromine, and is probably a mixture of lactonic acids. *Trimethyl homocamphoronate*, $C_7H_{13}(CO_2Me)_3$, was obtained on treating the acid with phosphorus pentabromide and bromine, and subsequently pouring into methyl alcohol; it boils at 305—308° under atmospheric pressure. *β-Anhydrohomocamphoronic acid*, $C_7H_{13}(CO_2H)\begin{matrix}CO\\CO\end{matrix}>O$, was obtained on allowing anhydrohomocamphoronic chloride to absorb moisture; it crystallises in well-formed plates or prisms melting at 128—129°; on treatment with aniline or *p*-toluidine, it affords an anilinic and a *p*-toluidinic acid identical with the substances obtained from the ordinary anhydro-acid. Camphononic acid could not be made to unite with hydrocyanic acid, remaining unaltered after several months' contact with the anhydrous acid. The *oxime* of camphononic acid, $CO_2H\cdot C_8H_{13}{:}N\cdot OH$, forms prisms melting at 178—180°; when warmed with sulphuric acid, it appears to undergo structural change, but the product affords camphoronic acid on oxidation.

By adding bromine to a solution of camphononic acid in chloroform, a *compound*, $C_8H_6Br_4$, is obtained, which crystallises in lustrous needles or prisms melting at 77—78°. It is probably a tetrabromoxylene.

***35. "Spectrographic studies in tautomerism. The absorption curves of the ethyl esters of dibenzoylsuccinic acid." By W. N. Hartley, F.R.S., and J. J. Dobbie, M.A., D.Sc.**

Knorr (*Annalen*, 1896, **293**, 70) describes three varieties of the ethyl ester of dibenzoylsuccinic acid. Two of these show exactly similar chemical reactions while they differ widely from one another in their solubility, melting points, and other physical properties. Knorr regards these bodies as stereoisomeric modifications of the "keto" form of the ester. The third ester differs from the two already referred to in its chemical as well as in its physical properties, and is regarded by Knorr as one of the three possible stereoisomeric modifications of the "enol" ester, or possibly as a mixture of the three modifications. His conclusions, which are based on purely chemical grounds, have been confirmed by the spectrographic examination.

Stereoisomerides, so far as they have been investigated, have shown no differences in the curves of molecular vibrations drawn from their absorption spectra, whereas substances having different constitutional formulæ have invariably different spectra. On applying this test to the ethyl esters of dibenzoylsuccinic acid, it was found that the "enol" ester gave a totally distinct spectrum from the "keto" esters, whilst the spectra of the "keto" esters were indistinguishable from one

another. The amount of general absorption caused by the "enol" ester is greater than that produced by the "keto" esters, and while all the esters exhibit selective absorption, the absorption band of the "enol" ester occupies a totally different position from the band of "keto" esters and is much less persistent.

The result of this investigation exemplifies the value of the spectrographic method, and shows how it might be applied with advantage to the investigation of similar cases of isomerism, either as a guide to the chemical investigation or to confirm the conclusions drawn therefrom, especially when any doubt arises as to whether the isomerides have a different constitution, or merely differ in the arrangement of the atoms in space.

***36. "The curves of molecular vibrations of benz-antialdoxime and benz-synaldoxime." By W. N. Hartley, F.R.S., and J. J. Dobbie, M.A., D.Sc.**

Benz-antialdoxime and benz-synaldoxime give identical curves of molecular vibrations. Ethereal solutions of the two substances were examined. A layer of either solution 25 mm. thick, containing 1 milligram-molecule in 100 c.c. of pure absolute ether, cut off all rays beyond $^1/\lambda$ 3323 ($\lambda = 3009$).

In a layer 1 mm. thick of a solution containing 1 milligram-molecule in 500 c.c. of ether, the spectrum is continuous to $^1/\lambda$ 3638 ($\lambda = 2748$), an absorption band making its appearance between $^1/\lambda$ 3638 ($\lambda = 2748$) and $^1/\lambda$ 4321 ($\lambda = 2314$), which is still discernible in a layer 1 mm. thick of a solution containing 1 milligram-molecule in 2500 c.c. of ether.

37. "On campholytic and isolauronolic acids." By James Walker and William Cormack.

A concentrated solution of potassium ortho-methyl camphorate yields methyl isolauronolate on electrolysis, and the purified isolauronolic acid obtained from this substance is optically inactive. The isolauronolic acid prepared from the campholytic acid of electrolysis is also without optical activity.

When campholytic acid is treated with fuming hydrobromic acid at the ordinary temperature, it speedily solidifies, forming the hydrobromide $C_8H_{14}Br \cdot CO_2H$, which melts with decomposition at about 100°, and is identical with the substance obtained by Noyes. Isolauronolic acid is attacked much more slowly by fuming hydrobromic acid, but eventually forms the same hydrobromide as campholytic acid. This hydrobromide, on treatment with alkali, decomposes according to the equations,

$$C_8H_{14}Br\cdot CO_2H + 2NaOH = C_8H_{13}\cdot CO_2Na + NaBr + 2H_2O.$$

Hydrobromide of Campholytic acid. — Sodium campholytate.

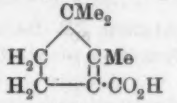
$$C_8H_{14}Br\cdot CO_2H + 2NaOH = C_8H_{14} + NaBr + NaHCO_3 + H_2O.$$

Isolaurolene.

These reactions serve to show that campholytic acid is an $\alpha\beta$-unsaturated acid, and that the bromo-acid melting at about 100° is its true hydrobromide. By means of them, isolauronolic acid may be transformed into campholytic acid, which, together with the isolaurolene obtained at the same time, is optically inactive.

When a more dilute hydrobromic acid is allowed to remain in contact with isolauronolic acid for a long time, a bromo-acid, $C_8H_{14}Br\cdot CO_2H$, is obtained which melts at 132° without decomposition. This is the true hydrobromide of isolauronolic acid, for on treatment with alkali this acid is regenerated from it.

The authors consider campholytic and isolauronolic acids to be stereoisomeric, their structure being best represented by the formula



derived from the Perkin-Bouveault formula for camphoric acid.

38. "The configuration of the camphoric acids." By James Walker and J. K. Wood.

l-Isocamphoric acid, prepared from *d*-camphoric acid by Marsh's method, has the dissociation constant $K = 0{\cdot}00160$ at 25°. When boiled with alcohol and a small quantity of sulphuric acid, it yields *ortho-ethyl* l-*isocamphorate*, m. p. 73·5°, $K = 0{\cdot}00065$, $[\alpha]_D = -46{\cdot}8$ for 10 per cent. solution in absolute alcohol. *Diethyl* l-*isocamphorate* is most easily prepared by heating dipotassium *l*-isocamphorate with excess of ethyl bromide in presence of ethyl alcohol for 5 hours at 100°, when a theoretical yield is obtained. It is an oil for which $[\alpha]_D = -50{\cdot}4°$ for 10 per cent. solution in absolute alcohol. *Allo-ethyl* l-*isocamphorate* is prepared by the half-saponification of the diethyl salt with the calculated quantity of alcoholic potash. It is a very viscous liquid, having $[\alpha]_D = -22{\cdot}9°$ for 10 per cent. solution in alcohol.

It is generally agreed that the molecule of camphoric acid contains two dissimilar asymmetric carbon atoms, which are links in a closed chain, and have attached to them the ortho- and allo-carboxyl groups respectively. On electrolysis of potassium allo-ethyl *d*-camphorate,

an ethereal product is obtained, the lowest boiling portions of which have only the allo-carboxyl group and the allo-asymmetric carbon atom, the ortho-asymmetric carbon atom having lost its asymmetry by the removal of the ortho-carboxyl group. This lowest boiling fraction has a strong positive rotation, namely $[\alpha]_D = +29{\cdot}8°$, which must be due to the allo-asymmetric carbon atom. If now the allo-asymmetric carbon atom of *l*-isocamphoric acid has the opposite configuration to that of *d*-camphoric acid, the rotation of the corresponding fraction from the ethereal product of electrolysis of potassium allo-ethyl *l*-isocamphorate should be of the same dimensions but of opposite sign, that is, it should be strongly negative. The rotation of the substance actually produced is, however, strongly positive, namely $[\alpha]_D = +20{\cdot}9°$, although the original substance and the impurities in the low boiling fraction have a large negative rotation. It appears, therefore, that the allo-asymmetric carbon atoms in *d*-camphoric acid and *l*-isocamphoric acid have the same configuration, and that the ortho-asymmetric carbon atoms have opposite configurations.

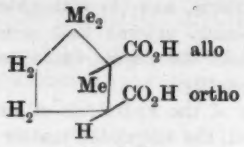
Assuming the configuration RR′ for ordinary camphoric acid, we can represent the configuration of all the camphoric acids by the following scheme :

	d-Camphoric.	*l*-Camphoric.	*d*-Isocamphoric.	*l*-Isocamphoric.
Ortho.....	R	L	R	L
Allo	R′	L′	L′	R′

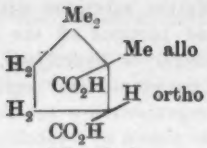
39. "The constitution of camphoric acid." By James Walker.

The Perkin-Bouveault formula for camphoric acid is considered by the author as the most satisfactory hitherto proposed. It represents camphoric acid as a derivative of succinic acid, and thereby accounts in a simple manner for the nature of the unsaturated compounds obtained by electrolysing the sodium alkyl salts of camphoric acid. In particular, the formulæ derived from it for campholytic and isolauronolic acids represent these substances as $\alpha\beta$-unsaturated acids without an asymmetric carbon atom, in accordance with their chemical behaviour and optical inactivity. Perkin's second formula and Bredt's formula, which represent camphoric acid as a derivative of glutaric acid, not only fail to explain the electrolytic production of campholytic and isolauronolic acids, but represent these acids as having an asymmetric carbon atom and therefore essentially active. Analogy and experiment alike exclude the assumption of a possible racemism.

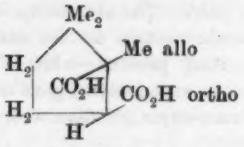
The configuration of the camphoric acids on the basis of the Perkin-Bouveault formula is as follows :



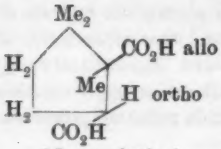
d-Camphoric.



l-Camphoric.



d-Isocamphoric.



l-Isocamphoric.

The dissociation constant of camphoric acid, which seems to be very small for a derivative of succinic or glutaric acid, is shown to be only apparently abnormal. The rise in the constant of succinic and glutaric acids when hydrogen is replaced by alkyl, is due to the approximation of the carboxyl groups, and is not the primary effect of the substitution. If the molecule acquires rigidity by ring formation or multiple linking, this approximation is prevented, and the primary effect of the substitution is observed, which is in general a diminution of the constant, as in monocarboxylic acids. It is therefore to be expected that the dissociation constant of camphoric acid, which has one tertiary and one secondary carboxyl, should be less than that of succinic or glutaric acids, which have two primary carboxyls. The very small values of the monocarboxylic acids derived from camphoric acid confirm this view.

40. "On the presence of invertase in plants of the Gramineæ. I." By James O'Sullivan.

The difficulty of extracting invertase from the living cells of plants which were proved to contain it was the first point considered. This was overcome in the following manner. Portions of the roots, culms and leaves of wheat, oats, and maize plants at various stages of growth, after being well washed with chloroform water, were digested in the cold, and at 49—50°, for different lengths of time, with a cane-sugar solution saturated with chloroform, and the amounts of cane-sugar hydrolysed were determined by the cupric oxide reducing power.

The amounts of cane-sugar hydrolysed are expressed in percentages of the weight of the portions of the plant with which it was digested, and these are taken as expressions for the invertase in those portions.

Check experiments made under similar conditions, (*a*) with cane-

sugar solution saturated with chloroform, and (*b*) with chloroform water and portions of the same plants, showed that practically no cane-sugar is hydrolysed, and that the cupric oxide reducing power of the extract is a negligible quantity.

That organisms are not the cause of the hydrolysis of the cane-sugar was proved by "catching up" all the suspended matter in the chloroform water used in washing the portions of the plants, either by means of aluminium hydrate or paper pulp. The aluminium hydrate deposit and the paper pulp, which would contain all the suspended matter—and consequently any organisms present—when digested with similar cane-sugar solutions as in the experiments, gave no more cupric oxide reducing power than the cane-sugar solution and chloroform alone.

41. "Iodonium compounds of the type $IR^{I}R^{II}R^{III}$ and the configuration of the iodine atom." By F. Stanley Kipping, Ph.D., D.Sc., F.R.S., and Harold Peters.

It has been shown by Hartmann and Victor Meyer (*Ber.*, 1894, **27**, 502, 1592) that diphenyliodonium hydroxide, $(C_6H_5)_2I\cdot OH$, is obtained when a mixture of iodosobenzene and iodoxybenzene is shaken with silver oxide and water; the authors have made use of this reaction for the preparation of iodonium bases containing different aromatic radicles.

Phenylparatolyliodonium hydroxide, $\begin{matrix}C_6H_5\\C_6H_4Me\end{matrix}\!\!>\!I\cdot OH$, is formed, together with its iodate, from a mixture of iodosobenzene and paraiodoxytoluene, $C_6H_5IO + C_6H_4Me\cdot IO_2 + AgOH = \begin{matrix}C_6H_5\\C_6H_4Me\end{matrix}\!\!>\!I\cdot OH + AgIO_3$, and is easily isolated in the form of its *iodide*, $\begin{matrix}C_6H_5\\C_6H_4Me\end{matrix}\!\!>\!I\cdot I$; this salt crystallises from boiling water in small, almost colourless needles and decomposes at about 153°.

A phenylparatolyliodonium iodide, identical in ordinary properties with the salt just mentioned, is obtained when a mixture of iodosoparatoluene and iodoxybenzene is treated with silver oxide and the product isolated as before.

The identity of these two preparations, if confirmed by further investigation, may be taken as showing that two of the three valencies of the iodine atom are symmetrically situated with respect to the third.

Attempts to resolve the phenylparatolyliodonium base into enantiomorphous components have so far been unsuccessful. When its iodide is treated with silver bromocamphorsulphonate in alcoholic solution, it is converted into *phenylparatolyliodonium bromocamphorsulphonate*,

$\begin{matrix}C_6H_5\\C_6H_4Me\end{matrix}\!\!>\!I\cdot SO_3\cdot C_{10}H_{14}OBr$, a compound which separates rom aqueous alcohol in highly lustrous, well-defined crystals, which contain water of crystallisation, and have in consequence an indefinite melting point.

The same salt is obtained from the two iodides which have been prepared by the different methods stated above.

When this phenylparatolyliodonium bromocamphorsulphonate is fractionally crystallised, the various deposits appear to be identical in ordinary and in optical properties; owing to the slight solubility of the salt in cold water, its specific rotation had to be determined in weak aqueous methyl alcohol, three different fractions giving $[\alpha]_D = +45°$, $+45°$, and $+47°$ respectively.

The samples of salt used contained about 3·6 per cent. of water, so that the molecular rotation of the anhydrous substance would be approximately $[M]_D = +283°$; other experiments showed that the presence of methyl alcohol has little effect on the specific rotation, so that, since the molecular rotation of the acid is $[M]_D = +270°$ in aqueous solution, it may be inferred that the iodonium base is optically inactive in all three fractions; unless, therefore, the bromocamphorsulphonate is a partially racemic salt, it may be provisionally concluded that the three iodine valencies, to which the several radicles are attached, are arranged in one plane.

The further investigation of the various points raised in this preliminary note is in progress.

42. "Note on the decomposition of semicarbazones." By F. Stanley Kipping, Ph.D., D.Sc., F.R.S.

In working with various semicarbazones, as, for example, with those of dimethylketohexamethylene, ketotetrahydronaphthalene, ketophenoheptamethylene, it was noticed that a brisk evolution of gas usually occurred when such compounds were melted, but that little if any charring took place. It seemed, therefore, that the decomposition products might be easily isolated, and that their examination would show the nature of the change which had occurred.

The only reference in the literature relating to this subject seemed to be that of Scholtz (*Ber.*, 1896, **29**, 610), who, in attempting to prepare pyridazine derivatives, discovered that the semicarbazones of methylethyl ketone and of other fatty ketones of low molecular weight were decomposed on dry distillation into ketazines and hydrazodicarbonamide.

The author finds that a similar change occurs in the case of the semicarbazones of aromatic compounds; when benzaldehyde semi-

carbazone, for example, is heated at a temperature above its melting point, it gives an almost theoretical yield of the *azine*, $C_6H_5\cdot CH{:}N\cdot N{:}CH\cdot C_6H_5$, the nature of which was established by direct comparison with the product of the interaction of benzaldehyde and hydrazine.

This formation of azines by the decomposition of semicarbazones seems also to take place in aqueous solution; when, for example, benzylparatolyl ketone is heated on the water-bath with an aqueous alcoholic solution of semicarbazide hydrochloride and sodium acetate, it seems to be converted in the first place into a colourless semicarbazone in the usual manner, but on continued heating the latter gradually changes into a canary-yellow product which is doubtless the *azine*, $\begin{matrix}C_6H_5\cdot CH_2\\ CH_3\cdot C_6H_4\end{matrix}\!\!>\!C{:}N\cdot N{:}C\!<\!\!\begin{matrix}CH_2\cdot C_6H_5\\ C_6H_4\cdot CH_3\end{matrix}$; the latter is readily soluble in chloroform, but only very sparingly so in hot alcohol, and separates from a mixture of these solvents in yellow needles melting at 172—173°.

It may be concluded from these experiments that the formation of azines from aromatic semicarbazones is also a fairly general reaction.

At the next meeting, on Thursday, March 15th, the following papers will be communicated by the authors:—

"The vapour densities of dried mercury and mercurous chloride." By H. Brereton Baker, M.A.

"The preparation of pure hydrobromic acid." By A. Scott, D.Sc., F.R.S.

"A new sulphide of arsenic." By A. Scott, D.Sc., F.R.S.

"The action of iodine on alkalis." By R. L. Taylor.

"The interaction between sulphites and nitrites." By Edward Divers and Tamemasa Haga.

"New polysaccharides: manno-galactan and lævulo-mannan." By Julian L. Baker and Thomas H. Pope.

RICHARD CLAY AND SONS, LIMITED, LONDON AND BUNGAY.

Issued 22/3/1900

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 16. No. 221.

March 8th, 1900. Extra Meeting. Professor THORPE, F.R.S., President, in the Chair.

Professor WARINGTON, F.R.S., delivered a Lecture on "Recent Researches on Nitrification."

During recent years, the chief investigations on the character and properties of the nitrifying organisms have been carried out in Winogradsky's laboratory in St. Petersburg, none having been executed in this country. Formerly, investigators had been unable to obtain pure cultures of the organisms; their chemical characters had, however, been studied, as their capacity for growth in a purely mineral solution allowed of their separation from most of the other organisms in the soil. It had been found that the process of nitrification consisted of two distinct pieces of chemical work, effected by two agents, which could be separated from each other; by the first (the nitrous organism), ammonia was converted into a nitrite; by the second (the nitric organism), the nitrite was oxidised to nitrate. These facts were first ascertained at Rothamsted.

To isolate the nitrous organism from soil, Winogradsky commences by a series of cultures in an inorganic solution containing an ammonium salt and the ash constituents of plant food. From this solution, cultivations on solid media are started. For some years, silica jelly was employed, but Oméliansky now prefers plates of magnesia-gypsum saturated with the mineral solution already mentioned. To isolate the nitric organism, the preliminary cultures are made in a solution containing sodium nitrite and ash constituents. As a solid medium, purified agar, with nitrite and ash constituents, is

made use of. The fermentable constituents of the agar have been previously removed by Beyerinck's method.

Winogradsky has examined soils from many parts of the world. He finds but one nitrous and one nitric organism in any soil. The nitric organism is everywhere the same species. The nitrous organism may vary. In Europe, N. Africa, and parts of Asia, the same species occurs, with variations in size, and in tendency to adopt a zoeglœa or motile condition; the latter condition displays the greater chemical energy. The nitrous organism from Java is a distinct species, having an extraordinarily long flagellum. The organism from S. America and Australia is generically different; it is a giant coccus. A few other investigators have described different nitrifying organisms, but the evidence adduced has in some cases proved erroneous, and is in other cases as yet insufficient to warrant its acceptance.

Winogradsky had proved by quantitative experiments that the nitrous organism derives its carbon from carbonic acid; the nitric organism possesses the same power. As both organisms flourish in darkness, the energy necessary for the construction of organic matter out of carbon dioxide and water is apparently derived from the oxidation, respectively, of ammonia or a nitrite. Later experiments have shown that the carbonic acid is, in every case, probably taken from a supercarbonate. The nutrition of the bacteria which exist with the nitrifying organisms in a mineral solution requires further study. Stutzer states that his hypomicrobium grows in a mineral solution, and needs carbonic acid for its nutrition, yet possesses no nitrifying power; its source of energy requires explanation.

The refusal of the nitrifying organisms to grow on gelatin, and on most organic media, is well known. Winogradsky and Oméliansky have lately studied the influence of various kinds of organic matter on the nitrifying process. The presence of 0·5 of glucose in 1000 of liquid is sufficient to retard the action of both the nitrous and nitric organism, while about 2 per 1000 entirely prevents nitrification. Glucose has thus as great an influence upon the nitrifying organisms as phenol has on ordinary bacteria. Of simpler forms of organic matter, as sodium acetate, a much larger quantity is required to hinder nitrification.

The influence of ammonia in preventing the action of the nitric organism is very remarkable; 5 parts per million was sufficient to retard its action, and 150 parts per million prevented it altogether, a proportion which is comparable with an effective dose of mercuric chloride. It seems, however, probable that an increase in the quantity and energy of the nitric organism enables it to bear a somewhat greater quantity of ammonia.

It appears from careful trials that the nitrifying organisms are without action upon nitrogenous organic matter; even methylamine is unaffected by them. For nitrification of organic matter to take place, the aid of other organisms is necessary to decompose it and bring the nitrogen into the form of ammonia. The behaviour of the nitrifying organisms towards organic matter and ammonia is of great practical importance.

The lecture was illustrated by lantern slides, and by a number of specimens of pure cultures on solid media, sent by Professor Winogradsky from St. Petersburg. The principal publications referred to will be found in *Trans. Chem. Soc.*, 1891, **59**, 484; *Archives des Sciences biologiques*, **1** and **7**; *Cent. Bakt.*, 1899, **2**, 652; *Mitt. Landw. Institute Breslau*, **1**, 75; **2**, 197; *Compt. rend.*, 1899, **128**, 566.

On the motion of Sir W. T. THISTLETON-DYER, seconded by Dr. HUGO MÜLLER, a vote of thanks was passed to Professor Warington for his lecture.

March 15th, 1900. Professor THORPE, F.R.S., President, in the Chair.

Messrs. A. H. Bennett, A. W. Harvey, and H. W. Cook were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Heinrich Rowland Beringer, 11, Dolcoath Road, Camborne; John Richard Brooke, 20, Aberdeen Park, Highbury, N.; Arthur Brand Chater, 65, Queen Street, Brisbane; Nicholas Cullinan, Risca, Monmouthshire; John Cussons, 4, Mount Pleasant, Portmadoc; William Donald, Saltcoats, Ayrshire; Frederic Richard Ellis, 15, Elton Road, Bishopston, Bristol; Thomas FitzGibbon, 1, Clyde Cottages, Ilford; James Herbert Haynes, 73, Brynland Avenue, Bishopston, Bristol; Thomas Lamb Lockhart, Johannesburg, Transvaal.

The following letter, addressed to the President, has been received from Professor van't Hoff, in acknowledgment of the congratulations sent to him by the Officers and Council on the occasion of the celebration, in December last, of the completion of the 25th year of his Doctorate:

CHARLOTTENBURG, 20*th February*, 1900.

MY DEAR COLLEAGUE,

Still engaged in answering the congratulations I received on the occasion of my Jubilee, I now come again to those from the Chemical Society of London, which reached me through the kind

intervention of you and Professor Dunstan. I pray that you will convey my feelings of gratitude to the Society, which has so recently admitted me as one of its Foreign Members.

I am, yours truly,

J. H. VAN'T HOFF.

Of the following papers, those marked * were read.

*43. "The vapour densities of dried mercury and mercurous chloride." By H. Brereton Baker, M.A.

The vapour density of ammonium chloride has already been shown to be normal when carefully purified and dried (*Trans.*, 1894, 65, 615; 1898, 73, 425), pointing to the fact that moisture is necessary for the dissociation of this substance. Experiments have been tried with purified and dried mercurous chloride with the view of finding out if it behaved in a similar way when vaporised. The determinations were made with a specially devised modification of Victor Meyer's apparatus in an atmosphere of nitrogen at 448°. The mean of five determinations gives a vapour density of 217·4. A determination of the vapour density of the undried substance in the same apparatus gave 118·4. Dried mercurous chloride did not give gold amalgam when gold was heated in its vapour. Under the same conditions, the gold amalgam was obtained with the incompletely dried chloride. Very dry mercurous chloride therefore would seem to have the formula Hg_2Cl_2 at 448°.

Similar experiments were made with carefully purified and dried mercury at 448°. The mean of three determinations in an atmosphere of nitrogen was 108·1, so that the molecule of dried mercury is probably monatomic at this temperature.

DISCUSSION.

Mr. D. HOWARD said that prolonged experience in the sublimation of large quantities of mercurous chloride had shown that the presence of vapour of water seemed to determine the corrosive action of the vapour on iron, and that the behaviour of the vapour of the chloride in the comparatively imperfect dryness obtainable on a large scale, suggested a true sublimation rather than dissociation.

Professor DEWAR remarked that it might interest the Society to know that Lord Rayleigh had recently found liquid air to be an effective desiccating agent as compared with phosphorus pentoxide, and that shortly the results of new determinations of the density of hydrogen thus dried would be communicated to the Royal Society.

Professor MCLEOD pointed out that it would be interesting to know

the quantity of water which would be sufficient to cause the complete dissociation of the heated mercurous chloride, for if the quantity were known it might be possible to ascertain the mechanism of the change.

***44. "The preparation of pure hydrobromic acid." By A. Scott.**

The author recommends the employment of sulphurous acid as a better and more convenient agent for preparing hydrobromic acid from bromine than amorphous phosphorus, even when purified from chlorides as Stas recommends. Almost all samples of phosphorus contain arsenic to a certain extent, and this, by the action of the bromine, becomes arsenious bromide which distils over with the hydrobromic acid, giving rise to arsenites and arsenates in the bromides prepared from acid made in this way.

By distillation two or three times, the hydrobromic acid is easily separated from the sulphuric acid formed at the same time, but it is always safer to add a little barium bromide before the final distillation. The purity of the acid was all that could be desired; this was shown by preparing from it some pure potassium bromide and titrating it against pure silver with all Stas's precautions, when its equivalent was found to be 119·099 (Ag = 107·93). Similar determinations with potassium bromide from hydrobromic acid prepared as recommended by Stas (*Œuvres*, 1, 842) and by J. P. Cooke (Squibb's process) (*Proc. Amer. Acad.*, 1881, 17, 31) gave 119·099 and 119·102 respectively. Stas's own number (mean of 14 experiments) is 119·095.

***45. "A new sulphide of arsenic." By A. Scott.**

When phosphorus containing (as it almost always does) small quantities of arsenic is oxidised by nitric acid and the solution boiled down, at a certain degree of concentration the liquid becomes brown provided too much nitric acid has not been used. This brown colour, as has long been known, is due to the separation of metallic arsenic by the reducing action of the phosphorous acid present. If, before the concentration has been carried so far, the liquid be diluted and sulphur dioxide passed into it and then warmed, a yellow precipitate of arsenic trisulphide is obtained, caused by the reduction of the sulphurous acid to hydrogen sulphide by the phosphorous acid. This reaction may be used as a test for arsenates by adding a few drops of phosphorus trichloride to the solution, then some sulphurous acid, and warming, when the yellow precipitate is obtained at once.

If, however, these substances be allowed to react at ordinary temperatures, a dark brown precipitate is obtained which consists almost entirely of a new arsenic sulphide having the formula As_2S. This

may be freed from the small quantity of trisulphide usually formed at the same time by repeated treatment with ammonia solution into which a little hydrogen sulphide has been passed. This new sulphide is unattacked by ammonia, colourless ammonium sulphide, or carbon disulphide, but dissolves in yellow ammonium sulphide and is attacked by potash solution, giving a dark brown substance exactly like that obtained by Berzelius by the action of potash solution on realgar.

***46. "The action of iodine on alkalies." By R. L. Taylor.**

In the present paper, the author describes experiments using iodine in much stronger solutions—decinormal—sixty times the strength of the aqueous solution previously used by him (*Mem. Lit. & Phil. Soc. Manch.*, 1897, 41, VIII.). Using Schwicker's method, he finds that if the requisite quantity (or more) of alkali is added to a decinormal solution of iodine and then a bicarbonate *immediately* added, from 88 to 94 per cent. of the iodine is liberated, and therefore that amount of the iodine had reacted with the alkali to form hypoiodite and iodide. By allowing different short intervals to elapse between the mixing of the alkali and iodine and the addition of the bicarbonate, he finds that the hypoiodite decomposes with great rapidity even at the ordinary temperature. The stability of a hypoiodite, in fact, depends upon its dilution, and this accounts for the definite results obtainable with very dilute solutions and the previous failures to obtain satisfactory evidence of the formation of hypoiodite when strong solutions of iodine, or the solid itself, have been used.

The iodine used was in solution in potassium iodide, the only effect of using varying amounts of which was to vary the amount of alkali required to complete the reaction, as might indeed be surmised from the fact that the reaction is a reversible one.

The author concludes that the action of iodine upon alkalies in the cold is always the same in the first instance, namely, the formation of hypoiodite and iodide, and that the hypoiodite decomposes more or less rapidly, according to the concentration, into iodate and iodide.

***47. "The interaction between sulphites and nitrites." By Edward Divers and Tamemasa Haga.**

The interaction of a nitrite with sulphurous acid or a sulphite, usually regarded as complicated, is really very simple. Nitrous acid, in the form of nitrous fumes, is entirely taken up by a solution of a pyrosulphite with the production of a two-thirds normal hydroximidosulphate, thus $HONO + (KSO_2)SO_3K = HON(SO_3K)_2$. If the normal sulphite be used, the reaction is $3HONO + 2K_2SO_3 = 2KNO_2 +$

$OH_2 + HON(SO_3K)_2$. Sulphurous and nitrous acids themselves may be used to show the nature of this interaction, and to prove that neither the base of the nitrite nor the sulphite takes any part in the sulphonation. A sulphite does not act on a nitrite in presence of free alkali, and a pyrosulphite ceases to act when it has become the normal sulphite by its action upon the nitrite. The sulphonation of a nitrite requires always an acidic condition of the solution, and the authors maintain that, in every case, it is nitrous acid itself, rather than the nitrite taken, which suffers the sulphonation. Carbon dioxide or an acid carbonate causes a normal sulphite to act slowly upon a nitrite.

The statements of Claus, Berglund, and Raschig, that an alkaline hydroxide is produced in the sulphonation of a nitrite, is disproved by the authors and shown to be due to a misconception of the facts observed.

Sulphur dioxide, passed into a solution of sodium or potassium nitrite and hydroxide, converts the latter into normal sulphite before sulphonation begins; pyrosulphite is then produced much faster than it can be consumed in sulphonating the nitrite, because of the retarding influence of the normal sulphite still present; and finally, when the quantity of the normal sulphite is sufficiently reduced, the pyrosulphite disappears faster than it is formed, leaving hydroximidosulphate as the sole final product. If the normal carbonate be taken in place of the hydroxide, the sulphonation proceeds rapidly with the simultaneous production of acid carbonate and of sulphite over and above what is consumed in forming the hydroximidosulphate, so long as any normal carbonate remains. Finally, the sulphite and acid carbonate are used up with the sulphur dioxide in sulphonating the last portions of the nitrous acid.

As it is nitrous acid itself which undergoes the sulphonation, the nitrite of any base should be capable of being used for the purpose, and the authors have tried with success, not only the nitrites of sodium and potassium, but also those of ammonium, calcium, barium, zinc, mercury (ous), and silver.

***48. "The sym-dipropyl-, sym-di-isopropyl-, and *aa'*-propylisopropyl succinic acids." By William A. Bone and C. H. G. Sprankling.**

In continuance of their investigations on the alkyl substituted succinic acids, the authors have prepared those which form the subject of the present communication, and show, contrary to the statement of Auwers (*Annalen*, 1898, **292**, 164), that each exists in two stereoisomeric, inactive forms.

In the case of each acid, each stereoisomeride yields with acetyl

chloride *its own* anhydride (liquid) which with aniline yields a characteristic anilinic acid; each isomeride, on being heated to a high temperature with strong hydrochloric acid under pressure, is to a greater or less extent converted into the opposite form; *trans*-acids are completely converted into *cis*-anhydrides on being heated with acetic anhydride to 170°.

The paper concludes with a discussion of the dissociation constants of the new acids in relationship to those of other alkyl-substituted succinic acids, special attention being drawn to the very great difference between the values for the *trans*- and *cis*-*s*-diisopropyl acids.

The chief properties of the acids may be thus tabulated:

	Trans.			*Cis.*		
	M. p. Acid.	M. p. Anilinic acid.	Dissociation constant.	M. p. Acid.	M. p. Anilinic acid.	Dissociation constant.
s-Dipropylsuccinic	182—3°	184—5°	0·025	121°	101—2°	0·049
s-Diisopropylsuccinic	226	201—2	0·0108	171	184—5	0·2300
$\alpha\alpha_1$-Propylisopropylsuccinic	192—4	147—9	0·0147	151—2	liquid	0·0295

49. "Manno-galactan and lævulo-mannan; two new polysaccharides." By Julian L. Baker and Thomas H. Pope.

The authors described two new complex carbohydrates, the one obtained from the Indian clearing nut (*Strychnos potatorum*), and the other from the ivory nut (*Phytelephas macrocarpa*). As these carbohydrates are very stable, the authors have been limited almost entirely to a study of the products obtained by their hydrolysis, these being, for the clearing nut substance, galactose and mannose, and for the ivory nut carbohydrate, mannose and another sugar, which, although not isolated as such, exhibits the characters of lævulose. Having regard to the relative proportions of the different sugars obtained, the authors propose to call the first of these substances manno-galactan, and the other lævulo-mannan. They give no colour reaction with iodine, nor could acetyl- or phenylhydrazine derivatives be obtained.

Manno-galactan.—The powdered clearing nuts are extracted with hot dilute aqueous alkali, and the filtered extract precipitated by means of Fehling's solution; this yields an insoluble, blue, pasty, copper compound, which, after washing, is decomposed with acid, the addition of alcohol to the acid solution then causing the reprecipitation of the carbohydrate. The manno-galactan thus prepared, when dry, is a

snow-white, amorphous substance, fairly soluble in cold water and more so in hot; it dissolves readily in dilute caustic alkali solutions. Its composition corresponds with the formula $C_6H_{10}O_5$, and in dilute aqueous solution it has a specific rotation $[\alpha]_D$ at 15° = +74°. After acid hydrolysis $[\alpha]_D$ has a value of about 58·8°, corresponding nearly with the proportion of two parts of galactose to one of mannose. This ratio is supported by the determination of the mucic acid yielded on oxidation with nitric acid. The *dibenzoyl* derivative, $C_6H_8O_5Bz_2$, of the manno-galactan is amorphous and dissolves in benzene, alcohol, and acetic acid, but gives no definite melting point; in a glacial acetic acid solution, its specific rotation $[\alpha]_D = +23°$.

Lævulo-mannan.—As this substance undergoes decomposition in contact with hot aqueous alkali, the extraction of the ivory nut turnings is carried out in the cold, the alkaline liquor being then precipitated by means of Fehling's solution. After separating and washing the copper compound, it is decomposed with hydrochloric acid, and the filtered acid liquid, on standing, deposits a thick, white precipitate, which is soluble in hot water, but on boiling the solution, the insoluble lævulo-mannan separates out. After drying, the lævulo-mannan is obtained as a white, amorphous substance having the composition $C_6H_{10}O_5$, and its specific rotation in dilute alkali $[\alpha]_D = -44·1°$. After hydrolysis with acid, $[\alpha]_D$ becomes +9·5°; this corresponds nearly with the proportion 20 parts of mannose to 1 of lævulose. Approximate determination of the mannose by the hydrazone method shows that at least 90 per cent. of the mixed sugars consists of mannose. The *dibenzoyl* derivative, $C_6H_8O_5Bz_2$, prepared by the Baumann method, is an amorphous substance soluble in benzene, alcohol, and glacial acetic acid, which has in the last-named solvent a specific rotation $[\alpha]_D = -74°$.

50. "Hydrolysis of semicarbazones." By George Young, Ph.D., and Ernest Witham, B.A., B.Sc.

The publication by Kipping of a "note on the decomposition of semicarbazones" (this vol., 63) necessitates a preliminary notice of an investigation on which the authors are engaged. Some time ago, they observed that hydrazodicarbamide gradually disappeared when boiled with water for some days, ammonia and carbon dioxide being evolved. By heating hydrazodicarbamide with water in a sealed tube, they were able to control the hydrolysis, and to obtain a solution the properties of which showed that it contained the first product of hydrolysis, ammonium semicarbazidocarboxylate, $NH_2·CO·NH·NH·CO_2NH_4$. When an aqueous solution of this salt is heated in an open vessel, it

rapidly dissociates into ammonia, carbon dioxide, and semicarbazide, the latter being then further hydrolysed.

The authors have studied the hydrolysis of other similarly constituted substances, amongst them benzalsemicarbazone. When boiled with water in a reflux apparatus, benzalsemicarbazone gradually acquires a yellow colour, due to the formation of benzalazine. Heated with water in a sealed tube, the benzalsemicarbazone dissolves to a colourless solution, which yields benzalazine on boiling, or more quickly on addition of sulphuric acid. In both cases, carbon dioxide is evolved. The filtrate from the benzalazine yields a further quantity of that substance on shaking with benzaldehyde.

The formation of benzalazine from benzalsemicarbazone when the latter is boiled with water takes place apparently according to the following scheme :

$$C_6H_5\cdot CH{:}N\cdot NH\cdot CO\cdot NH_2 + H_2O = C_6H_5\cdot CH{:}N\cdot NH\cdot CO_2NH_4.$$
$$C_6H_5\cdot CH{:}N\cdot NH\cdot CO_2NH_4 = C_6H_5\cdot CH{:}N\cdot NH_2 + CO_2 + NH_3.$$
$$2\,C_6H_5\cdot CH{:}N\cdot NH_2 = C_6H_5\cdot CH{:}N\cdot N{:}CH\cdot C_6H_5 + N_2H_4.$$

In the formation of the azine from benzylparatolylketone, quoted by Kipping, the process would doubtless be hastened by the presence of free acetic acid.

The investigation is being extended to the corresponding thio-compounds and to substituted hydrazodicarbamides.

51. "The dissociation constant of azoimide." By Charles Alfred West, A.R.C.Sc.

The dissociation constant of azoimide in aqueous solution was determined some years ago by Ostwald, but no details were ever published. The results obtained by the author agree closely with those of Ostwald, and show that azoimide as an acid approximates to acetic acid. The values of μ, m, and k are as follows :

v.	μ.	m.	k.
10	5·38	0·01397	0·0000198
100	15·98	0·0415	0·0000180
1000	45·97	0·1194	0·0000166

52. "Racemisation occurring during the formation of benzylidene, benzoyl and acetyl derivatives of dextro-ac-tetrahydro-β-naphthylamine." By William Jackson Pope and Alfred William Harvey.

On heating dextro-ac-tetrahydro-β-naphthylamine carbonate (*Proc.*, 1899, 15, 170) with benzaldehyde on the water-bath, a product is

obtained which by fractional crystallisation is resolved into the inactive benzylidenetetrahydro-β-naphthylamine of Bamberger and Kitscheldt (*Ber.*, 1890, **23**, 876) and *benzylidenedextrotetrahydro-β-naphthylamine*, $C_{10}H_{11}\cdot N{:}CHPh$; the new substance, which is accompanied by about 20 parts of the isomeride, crystallises in aggregates of colourless needles melting at 58—60°, and since it is more soluble than the inactive isomeride, the latter is a true racemic compound. The purest sample obtained of the active substance has $[\alpha]_D = +27{\cdot}6°$ in a 1 per cent. solution in alcohol.

Benzoylation occurs readily on treating dextrotetrahydro-β-naphthylamine dextro-α-bromocamphorsulphonate by the Schotten-Baumann method, but the product consists almost wholly of the inactive benzoyltetrahydro-β-naphthylamine of Bamberger and Müller (*Ber.*, 1888, **21**, 850), and contains only a very small proportion of *benzoyldextrotetrahydro-β-naphthylamine*, $C_{10}H_{11}\cdot NH\cdot COC_6H_5$; a larger yield of the latter substance is obtained by adding a solution of benzoic chloride in benzene to a solution of dextrotetrahydro-β-naphthylamine in benzene at 0°. The active benzoyl derivative is isolated by fractional crystallisation from alcohol, being more soluble than its inactive isomeride, and forms less than 5 per cent. of the total product. It crystallises in wool-like needles melting at 155—157°, and the highest specific rotation observed was $[\alpha]_D = +58°$ in solution in acetone.

On treating at 0° a solution of dextrotetrahydro-β-naphthylamine in benzene with acetyl chloride dissolved in benzene a mixture of Bamberger and Müller's inactive tetrahydroacenaphthalide with 2 or 3 per cent. of *dextrotetrahydroacenaphthalide*, $C_{10}H_{11}{:}NH\cdot COCH_3$, is obtained; the active component is the more soluble, and may be isolated by fractional crystallisation from benzene. It forms long, colourless needles melting at 104—106°, and the highest specific rotation observed was $[\alpha]_D = +37°$ in a 2 per cent. solution in benzene.

During the conversion of dextrotetrahydro-β-naphthylamine into its benzylidene, benzoyl, or acetyl derivative, all but a very small proportion of the primary base undergoes racemisation, and this racemisation apparently occurs prior to the formation of the final product, because the active derivatives are not racemised by heating at 100° either alone or in solution. Racemisation, as a result of operating upon an amido-group contiguous to an asymmetric carbon atom, does not seem to have been observed before, most of the cases, with rare exceptions, such as that of camphor (Kipping and Pope, *Trans.*, 1897, **71**, 956), being of substances in which a hydroxyl-group is attached to the asymmetric carbon atom, and in which the possibility arises of change from an "enolic" to a "ketonic" form. It is important to note that in the present cases the whole of the material

is not racemised, indicating that the asymmetric carbon atom in the group $\begin{matrix}\cdot CH_2\\ \cdot CH_2\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}H\\ NH_2\end{matrix}$ never becomes separately bound to only three atomic groups at any stage in the substitution.

Work on these and analogous cases is being continued in the hope of obtaining information respecting the mechanism of substitution in trivalent nitrogen compounds.

ANNUAL GENERAL MEETING.

BUNSEN MEMORIAL LECTURE.

The Annual General Meeting of the Society, for the election of Officers and other business, will be held on Thursday, March 29th, at 3 o'clock in the afternoon.

At this meeting the Longstaff Medal will be presented to Professor W. H. Perkin, junr., F.R.S.

In the evening, the Bunsen Memorial Lecture will be delivered by Sir Henry E. Roscoe, F.R.S., Vice-President The Chair will be taken at 8.30.

At the next ordinary meeting, on Thursday, April 5th, the following papers will be communicated by the authors.

"The liquefaction of a gas by 'self-cooling.' A lecture experiment." By G. S. Newth.

"Note on partially miscible aqueous inorganic solutions." By G. S. Newth.

"The decomposition of chlorates. Part II." By W. H. Sodeau, B.Sc.

RICHARD CLAY AND SONS, LIMITED, LONDON AND BUNGAY.

Issued 11/4/1900

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 16. No. 222.

March 29th, 1900. Annual General Meeting. Professor THORPE, F.R.S., President, in the Chair.

Dr. DYER and Mr. FRISWELL were appointed Scrutators, and a ballot was opened for the election of Officers and Council for the ensuing year, the ballot being closed at the conclusion of the President's address.

In beginning his Address, the President congratulated the meeting on the fact that the Society continues to grow and prosper; the number of its Fellows steadily increases, and their communications continue to add to its dignity and usefulness. Its financial position is no less satisfactory.

The numerical strength of the Society was as follows:—

Number of Fellows, March 29th, 1899		2230
,, ,, since elected		118
,, ,, reinstated by Council		4
		2352
Removed on account of non-payment of two annual subscriptions	15	
Withdrawn	20	
Deaths	25	60
Number of Fellows, March 29th, 1900		2292
Foreign Members		33

The names of those removed were :—Eugen Blume ; Rev. J. Campbell ; J. E. Foakes ; Bertram Hunt ; H. Hyatt ; J. D. Johnstone ; C. L. Kennicott ; H. A. Lawrance ; W. J. Martin ; K. P. McElroy ; T. G. Nicholson ; J. H. Overton ; A. E. Potter ; John Provis ; J. Wrightson.

The following have withdrawn :—Henry Austin Appleton ; Howard Barrett ; Claude H. Bater ; Richard A. Bush ; G. W. Davies ; Alfred George Earl ; J. M. Fallon ; W. A. Greaves ; H. Loft Haller ; M. Holzmann ; A. Wentworth Jones ; John Temple Leon ; E. W. Lucas ; Prosper H. Marsden ; Walter George McMillan ; T. Ormerod ; J. R. Skelton ; Edward Smith ; Henry J. Staples ; Claude T. Vautin.

The following have died :—Joshua Buchanan ; Robert Wilhelm Bunsen ; Kanny Lall Dey ; J. B. Edwards ; Sir Edward Frankland ; Charles Friedel ; William Harkness ; John F. Hodges ; John Elias Hughes ; Eric H. Jackson ; William Marcet ; Alexander McDougall ; Walter Newton ; L. F. Nilson ; G. H. Ogston ; Robert Oxland ; R. T. Plimpton ; C. F. Rammelsberg ; Henry Charles Reynolds ; J. G. F. Richardson ; W. H. Richardson ; Thomas Glazebrook Rylands ; Edward C. Cortis Stanford ; Sidney Augustus Sworn ; Andrew Taylor ; William Thorp ; Ferdinand Tiemann ; Peter Waage ; David Watson ; W. Lloyd Williams.

The passing away of so eminent a member of the Society, and of one who played such a leading part in the development of chemistry, as Sir Edward Frankland is no ordinary event in the history both of Science and of the Society, and demands a special reference. The Council have accordingly determined that Sir Edward Frankland's services shall be commemorated in the manner hitherto restricted, with the special exception of the late Professor von Hofmann, to its Honorary Foreign Members ; and they have requested his pupil, collaborator, and friend, Professor Armstrong, to give a Memorial Lecture on his life-work in the ensuing autumn.

The names of the deceased Foreign Members are Robert Wilhelm Bunsen, Charles Friedel, Lars Fredrik Nilson, Carl Friedrich Rammelsberg, and Peter Waage.

Bunsen, who was elected a Foreign Member during the first session of the Society, namely, as far back as February 1, 1842, and who was long the *doyen* on the list, died on August 16, 1899, in his 89th year. His friend and pupil, Sir Henry Roscoe, a past President of the Society, has undertaken, at the request of the Council, to commemorate the signal services which Professor Bunsen rendered to physical science

Charles Friedel, Member of the Institute and Professor of Chemistry in the Sorbonne, who was elected a Foreign Member of the Society on May 18th, 1876, died on April 20th, 1899, at the age of sixty-seven. His friend and co-worker, Professor J. M. Crafts, of the Massachusetts Institute of Technology, and a Fellow of this Society, has kindly responded to the invitation of the Council to prepare a Memorial Lecture, which he hopes to be able to deliver on some evening in the latter half of June next.

Lars Fredrik Nilson, Professor of Agricultural Chemistry in the Kongl. Landtbruks-Akademien, Stockholm, and formerly Professor of Analytical Chemistry in the University of Upsala, whose name is specially connected with the chemistry of the so-called rare earths, and who was elected a Foreign Member of the Society on February 2, 1888, died on May 14, 1899, in his 59th year. Professor Otto Pettersson, of the Free University of Stockholm, who was associated with Nilson in most of his work in pure chemistry, has undertaken, in compliance with the wish of the Council, to give the Society an account of the many services which his friend rendered to chemistry, and he hopes to be able to visit London for this purpose in the first week of July next.

Carl Friedrich Rammelsberg, Geh. Reg. Rath. and Emeritus Professor of Inorganic Chemistry in the University of Berlin, who was elected a Foreign Member on May 3, 1866, died on December 28, 1899, in his 87th year. Professor H. A. Miers, of Magdalen College, Oxford, and a Fellow of this Society, has kindly acceded to the wish of the Council to prepare a memorial lecture on the life-work of the veteran mineralogical chemist, which he hopes to deliver to the Society in December next.

Peter Waage, Professor of Chemistry in the University of Christiania, whose name is best known in connection with the studies on chemical affinity which he made in association with his colleague, Professor Guldberg, died on January 13th of this year. He was elected a Foreign Member of this Society on January 20th, 1898.

Since the last Anniversary, 175 communications have been made to the Society, a number greater than in any preceding year. In character, variety, and importance they compare not unfavourably with the contributions of any former period. Abstracts of all these have appeared in the *Proceedings*, and 83 have already been published in the *Transactions*. The volume of *Transactions* for 1899 contains 120 memoirs, occupying 1166 pages; in the preceding year 102 papers were published, occupying 1038 pages.

The volumes for 1899 contain 3617 abstracts of papers, published mainly in Continental journals, occupying 1796 pages, arranged as follows:

PART I.

	Pages.	No. of Abstracts.
Organic Chemistry	968	1477

PART II.

General and Physical Chemistry		421
Inorganic Chemistry		417
Mineralogical Chemistry		211
Physiological Chemistry		236
Chemistry of Vegetable Physiology and Agriculture		244
Analytical Chemistry		611
	828	2140
Total in Parts I. and II.	1796	3617

The number of abstracts dealt with in 1899 is 791 more than in the preceding year. All arrears in abstracting have at length been overtaken. The Fellows may now count upon having the monthly *résumé* of contemporary chemical literature brought to their attention as quickly as it is possible to furnish it.

It will have been observed also that the Editor has succeeded in issuing the Journal somewhat earlier in the month than has hitherto been thought possible.

The question of co-operation with other English-speaking Chemical Societies in the preparation of abstracts of foreign chemical literature was referred to in the last Presidential Address. But, although the matter has been considered, the Committee appointed to deal with this question has not yet reported.

637 copies of the 1883–92 Index and 317 of the 1873–82 Index were issued to Foreign Members, Institutions, and to those Fellows who, being entitled to a Free Grant of them, had made application within the prescribed period. 565 of these applications had been received, of which 43 were those of Fellows resident abroad.

The work of compilation of the Collective Index showed the necessity of indexing the annual volumes in a more systematic manner than had been done in the past. For the last four years, the work of indexing the annual volumes has been entrusted to a special staff of indexers under the direction of the Sub-Editor. This plan has worked well as regards uniformity and consistency, but unfortunately it has not been possible, by means of it, to bring out the Annual Index with that promptitude which is desirable. The Index Committee has therefore suggested to the Council the propriety of entrusting the work of

indexing to one person, to be responsible, under the direction of the Editor, for the preparation and speedy publication of the work, and the Council has sanctioned the employment, on this work, of Mrs. Dougal, who is already favourably known to the Fellows for the excellent service she rendered the Society in editing the Collective Indexes of its publications since 1873.

The Fellows are aware the Society stocks a certain number of its publications, and the question of the custody and supply of back numbers has received attention. A limited number of sets of the *Memoirs* and *Proceedings* of 1841—7, of the *Quarterly Journal*, 1849—62, and of the First Series of the *Journal* from 1863 onwards are now on sale.

As regards the Library, 790 books have been borrowed, as against 727 last year; and 114 books, 397 volumes of periodicals, and 27 pamphlets have been added, as against 67 books, 285 volumes of periodicals, and 24 pamphlets in the preceding year.

The condition of the Library Catalogue has received attention, and the Council has directed a new Catalogue to be prepared according to a scheme drawn up by the Library Committee; and the work is well advanced under the direction of Mr. Steele, assisted by Miss Morfee.

Grants amounting to £192 have been made in aid of chemical investigation.

The Longstaff Medal has been awarded to Professor W. H. Perkin, F.R.S. In making the presentation, the President said :—

"Dr. Perkin, it gives me a special pleasure to ask you, on behalf of the Chemical Society, to transmit this medal to your son, Professor W. H. Perkin, who, to our great regret, is unable to be here to receive it in person. The Longstaff Medal has been awarded to him for his researches on closed chain compounds of the trimethylene and similar series, and for his recent important syntheses of camphor derivatives.

"The Council desire on making this award to indicate how highly we regard the contributions with which he has enriched our *Transactions*. Under his stimulating influence, the chemical laboratory of the Owens College, and especially that section of it under his more immediate direction, continues, as of old, to furnish a succession of valuable memoirs to English chemical literature. We trust that this activity may long be maintained, and that our Society may continue, as in the past, to enjoy the credit and distinction of disseminating the results of the inquiries to which his fruitful ideas give rise."

During the long vacation, the building has been thoroughly cleaned and redecorated, and certain much needed improvements in the lavatory accommodation and in the sanitary arrangements of the building have been effected.

The accommodation at the disposal of the Society is, however, a

matter of growing concern. The meeting-room seats no more than 157 persons, in spite of the increased space which was gained as the results of the alterations in 1892. This is altogether incommensurate with the present numerical strength of the Society, and, as the Fellows well know, considerable inconvenience is occasionally felt owing to the impossibility of finding room for those who wish to attend the meetings. The collection of books is gradually overspreading into every room the Society possesses and such conveniences as the officers have for the discharge of their official business and for the custody of the official records are greatly curtailed by the increasing inadequacy of the space at their disposal.

The Society is indebted to several of its Fellows for additions to its artistic possessions; among these is a bust of Sir Humphry Davy, presented by Dr. Debus, a copy of which in bronze, together with its pedestal, has been given by Dr. Messel; Dr. Atkinson has presented an electrotype medallion of Wöhler, executed by Dr. Hugo Müller, and Sir Henry Roscoe has given some photographic mementoes of his association with Bunsen and the Heidelberg Laboratory.

The Society had the pleasure of congratulating, by a suitable address, Sir George Gabriel Stokes on the occasion of his jubilee as Lucasian Professor of Mathematics, and it has since received from the University of Cambridge an exemplar of the medal which was struck in commemoration of that event.

Congratulations have also been sent to Professor Emil Fischer and Professor van't Hoff on the twenty-fifth anniversaries of their doctorates, of which acknowledgments, already published in the *Proceedings*, have been received.

The remainder of the address was devoted to a review of the progress of chemical science from the beginning of the century to the date of the formation of the Society.

Sir H. Roscoe, F.R.S., proposed a vote of thanks to the President, coupled with the request that he would allow his address to be printed in the *Transactions*.

Prof. Liveing, F.R.S., seconded the motion, which was carried by acclamation.

The President having returned thanks,

Prof. Tilden, F.R.S., the Treasurer, in giving an account of the Balance Sheet which he laid before the Society, duly audited, said:—

The receipts had been:—By admission fees and subscriptions, £4088; by sale of Journal and advertisements, £781 15*s.* 6*d.*; and by dividends on invested capital, £444 13*s.* 7*d.* The expenses had been:—On account of the Journal, £3388 12*s.* 11*d.*; on account of the Proceedings, £171 14*s.* 7*d.*; on account of the preparation of a new Card Catalogue, £35 9*s.* 2*d.*; on account of the Library, £286 17*s.* 3*d.*;

House expenses, including the re-decoration of the Building, £543 5*s.* 11*d.*; the total expenditure being £4993 13*s.* 1*d.* Grants amounting to £192 had been made to Fellows from the Research Fund during the year.

Attention was directed to the fact that the net income of the Society for the year being £5,371 1*s.* 5*d.*, and the expenses £4,993 13*s.* 1*d.*, the surplus is only £377 8*s.* 4*d.* This is considerably less than the amount, £578, of the Composition and Admission Fees which ought to be regarded as Capital. In view of the steadily increasing cost of the Society's publications, the recurrence of the heavy charge for the Decennial Index, and the growth of the Library, economy will have to be practised to keep the finances of the Society in a healthy condition. The Treasurer appealed to authors of papers to assist in keeping down the cost of the composing and correcting the proofs of papers communicated to the Society. At the present time the average cost of corrections amounts to more than one-third the charges for putting manuscript into type. A little more care exercised by authors in preparing for the press would result in a substantial reduction in the cost of printing.

The Treasurer, in concluding, proposed a vote of thanks to the auditors, which was acknowledged by Mr. Page.

Prof. Odling, F.R.S., proposed that the thanks of the Fellows be tendered to the Treasurer for his services during the past year; this motion was seconded by Dr. Russell, F.R.S., and carried.

Prof. H. B. Dixon, F.R.S., proposed a vote of thanks to the Officers and Council.

Prof. Warington, F.R.S., seconded the motion, which was unanimously adopted.

Prof. Dunstan, F.R.S., responded on behalf of the Council.

Prof. Dewar, F.R.S., proposed a vote of thanks to the Editor, Sub-Editor, Abstractors, and Indexers, which was seconded by Mr. Groves, F.R.S., and carried.

Dr. Wynne, F.R.S., responded.

The Scrutators having presented their report to the President, he declared that the following had been duly elected :—

President: T. E. Thorpe, Ph.D., D.Sc., LL.D., For.Sec.R.S.

Vice-Presidents who have filled the office of President: Sir F. A. Abel, Bart., K.C.B., D.C.L., F.R.S.; H. E. Armstrong, Ph.D., LL.D., F.R.S.; A. Crum Brown, D.Sc., LL.D., F.R.S.; Sir W. Crookes, F.R.S.; James Dewar, M.A., LL.D., FR.S.; Sir J. H. Gilbert, Ph.D., LL.D., F.R.S.; J. H. Gladstone, Ph.D., D.Sc., F.R.S.; A. Vernon Harcourt, M.A., D.C.L., F.R.S.; H. Müller, Ph.D., LL.D., F.R.S.; W. Odling, M.B., F.R.S.; W. H. Perkin, LL.D., Ph.D., F.R.S.; Sir H. E. Roscoe,

D.C.L., LL.D., F.R.S.; W. J. Russell, Ph.D., F.R.S.; A. W. Williamson, LL.D., F.R.S.

Vice-Presidents: E. Divers, M.D., D.Sc., F.R.S.; C. E. Groves, F.R.S.; G. D. Liveing, M.A., D.Sc., F.R.S.; T. Purdie, Ph.D., F.R.S.; T. Stevenson, M.D.; John M. Thomson, LL.D., F.R.S.

Secretaries: Wyndham R. Dunstan, M.A., F.R.S.; A. Scott, M.A., D.Sc., F.R.S.

Foreign Secretary: Raphael Meldola, F.R.S.

Treasurer: William A. Tilden, D.Sc., F.R.S.

Other Members of Council: H. Brereton Baker, M.A.; F. D. Chattaway, Ph.D., D.Sc.; Frank Clowes, D.Sc.; J. Norman Collie, Ph.D., F.R.S.; A. E. Dixon, M.D.; H. J. H. Fenton, M.A., F.R.S.; W. Gowland; C. T. Heycock, M.A., F.R.S.; D. Howard; Rudolph Messel, Ph.D.; W. J. Pope; James Walker, D.Sc.

March 29th, 1900. Extra Meeting. Professor Thorpe, F.R.S., President, in the Chair.

Sir Henry E. Roscoe, F.R.S., Vice-President, delivered the Bunsen Memorial Lecture.

Before commencing the Lecture, Sir Henry Roscoe read the following telegram, which he had just received from Bunsen's nephew and executor, Dr. Philipp Bunsen, of Marburg. "On the occasion of the Memorial Lecture, the Bunsen family joins sincerely with the illustrious Society, and sends respectful thanks and compliments."

The death of Bunsen on August 16th, 1899, severs the last link connecting the chemists of our time with the great men of the earlier part of the century, Berzelius, Gay Lussac, Dumas, Liebig, and Wöhler, Mitscherlich and the two Roses, as well as with the physicists Dove, Wilhelm Weber, and Magnus, all of whom he counted amongst his personal friends. Living to the ripe age of 88 years, he was destined to witness the deaths as well as the scientific births of many distinguished colleagues and pupils; of Kirchhoff, Helmholtz, Kopp, and Hermann; of Strecker, Kolbe, Kekulé, Pebal, Lothar Meyer, and, finally, of Victor Meyer, his successor in the chair at Heidelberg.

Robert Wilhelm Bunsen was born on March 31st, 1811, at Göttingen, where his father was chief University Librarian and Professor of Modern Philology. Entering the University in 1828, he

studied chemistry under Stromeyer, and graduated in 1830. He then visited Paris, Berlin, and Vienna, continuing his studies and making the acquaintance of the scientific men of those cities, returning to Göttingen, where, in 1834, he was admitted by the University as Privatdozent in Chemistry. In 1836 he succeeded Wöhler as teacher of chemistry in the Polytechnic School at Cassel, and in 1839 was appointed Professor Extraordinarius of Chemistry at Marburg, being advanced in 1842 to the post of Ordinarius. Here he remained till 1851, when he went for a short period to Breslau, and in 1852 he accepted the chair at Heidelberg, which he occupied until his retirement in 1889. In these several positions, Bunsen laboured incessantly and devotedly for 56 years in the furtherance of chemical science, with the result that his name will be handed down to posterity as one whose work has earned for him the very first rank amongst chemists of the nineteenth century.

Bunsen's first published paper recorded his discovery that freshly precipitated ferric hydroxide acted as a powerful antidote in cases of arsenical poisoning, but the first research in which he showed his power was the classical one on the cacodyl compounds, which was continued for no less than six years. His important investigations on the composition of the gases of German and English blast-furnaces were of the highest practical as well as theoretical importance, and led incidentally to the devising and perfecting of his well-known system of gas analysis. In 1857, he collected in a volume the whole of his gasometric researches, and of this—the only book he ever published—a second and greatly enlarged edition appeared in 1877.

The construction of his carbon-zinc battery marks an era in the economic production of electricity. He showed how it could be employed as a means of illumination; he determined its power of doing work, and used it to prepare electrolytically many metals hitherto unknown in a coherent form, notably magnesium, the preparation of which had baffled Davy. These researches led in turn to his inventions of the well-known "grease spot" photometer and the ice- and the vapour-calorimeters. Along with the lecturer, he carried out the photochemical researches based on the action of light on a mixture of equal volumes of hydrogen and chlorine, pronounced by Ostwald to be "the classical example for all further researches in physical chemistry."

The famous researches on spectrum analysis of Kirchhoff and Bunsen gave, not only a full explanation of Frauenhofer's lines in the solar spectrum and a knowledge of the composition of the sun and the fixed stars, but led in Bunsen's hands to the discovery of two new metals, cæsium and rubidium, and in the hands of others, of thallium, indium, gallium, and other elements.

In 1846, Bunsen spent $3\frac{1}{2}$ months in Iceland, as a member of an expedition promoted by the Danish Government, of which the

outcome was his well-known series of investigations of the volcanic and pseudo-volcanic phenomena of that island. He worked for some time at the separation of the metals in the residues left after the extraction of the platinum, as carried out in the Imperial Mint at St. Petersburg, and in his account of this work is to be found a description of his filter pump actuated by a fall of water.

To Bunsen and Schischkoff we owe the first exact examination both of the gaseous and solid products of the explosion of gunpowder. Perhaps his name is most widely known in connection with his burner for gas, devised to provide a flame both hotter and more steady than that of the argand burner with wire-gauze top previously in use. Not only as a source of heat, but also most ingeniously as an analytic agent, was the flame of his gas burner employed in producing the delicate and characteristic "flame reactions." Important also are his papers on the colour of water, iodometric methods, and water analysis.

The remainder of the Lecture consisted of the lecturer's personal recollections of Bunsen, and of the Heidelberg Laboratories from 1852 onwards, with a description of the character and methods of work of the Master as a teacher and a lecturer, and of the relations existing between him and his pupils.

Considerate and generous towards the opinions of others, he held firmly to his own, which at times he did not fail strongly to express; simple and straightforward, he disliked assumption and hated duplicity; single-minded and wholly devoted to his science, he abhorred vanity and despised popularity hunting.

At the time of his death, Bunsen had been for many years our senior Foreign Member, having been elected on February 1, 1842, during the first session of our Society. In 1858 he became a Foreign Fellow of the Royal Society, and in 1860 the Copley Medal was awarded to him. To Bunsen and Kirchhoff, in 1877, the first award of the Davy Medal was made in recognition of their researches and discoveries in spectrum analysis.

Another English honour conferred upon him was that of the award in 1898 of the Albert Medal of the Society of Arts, given for "distinguished merit in promoting art, manufactures, or commerce," in recognition of his numerous and most valuable applications of chemistry and physics to the arts and to manufactures.

On the motion of Professor ODLING, seconded by Dr. E. ATKINSON, a vote of thanks was passed to Sir HENRY ROSCOE for his Lecture.

April 5th, 1900. Professor J. M. THOMSON, F.R.S., Vice-President, in the Chair.

Certificates were read for the first time in favour of Messrs. James Ashton, Land Hill House, Hoscar Moss, Ormskirk, Lancs.; Richard

Henry Cyril Gompertz, 110, Elgin Crescent, Notting Hill, W., Alexander Ernest McKensie, 11, Bank Road, Workington; Hugh McNair, Bellfield, Wishaw; Herbert Procter Smith, 60, Stepney Street, Llanelly; George Edward Tomlins, 4, Radford Road, Hither Green, London, S.E.

Of the following papers, those marked * were read.

***53. "The liquefaction of a gas by 'self-cooling' (a lecture experiment)." By G. S. Newth.**

The principle of the modern method for obtaining liquid air or oxygen by the "regenerative" method may be illustrated for lecture purposes by means of nitrous oxide, the spiral of fine copper tube, being attached directly to the steel bottle containing nitrous oxide, and inserted into a Dewar vacuum-jacketed test-tube. No other insulating arrangements are required. In order to maintain the necessary pressure in the nitrous oxide bottle, the latter is kept in warm water at a temperature of about 30°.

***54. "Note on partially miscible aqueous inorganic solutions." By G. S. Newth.**

When strong aqueous ammonia (sp. gr. 0·880) is added to a saturated solution of potassium carbonate and the liquids shaken together, two distinct layers separate out, just as in the case of water and ether. At ordinary temperatures, it is found that the potassium carbonate solution dissolves about 37 per cent. of the ammonia solution, while the latter dissolves about 6 per cent. of the potassium carbonate solution by volume.

The solubility of each liquid in the other increases with rise of temperature, the curves of their solubilities intersecting at 43°, above which temperature the solutions are miscible in all proportions. A small amount of added water is also found to increase the mutual solubility; with 12·9 per cent. of added water, the separate phases cease to exist above 10°, whilst if 18·1 per cent. of water be added, the liquids are miscible in all proportions at all temperatures above 0°. When cooled below these critical temperatures, the clear solution instantly becomes turbid by the separation into two liquids. No other aqueous solutions of inorganic substances have as yet been found which exhibit a similar behaviour, but strong aqueous solutions of trimethylamine and triethylamine behave in a like manner with a saturated solution of potassium carbonate.

Discussion.

Dr. Divers said that Mr. Newth's paper was interesting on account of the evidence it afforded that we had in aqueous ammonia an analogue of aqueous alcohol, the liquefied ammonia precipitating salts from aqueous solution and becoming dehydrated by potassium carbonate. He had himself shown that ammonium nitrate deliquesced in ammonia gas just as other salts deliquesced in aqueous vapour, and then furnished liquid ammonia under atmospheric pressure, which behaved as a solvent like water or alcohol.

***55. "The decomposition of chlorates. Part II. Lead chlorate." By William H. Sodeau, B.Sc.**

The preparation of pure anhydrous lead chlorate and the examination of the products of its slow decomposition were first dealt with. The solid residue was found to absorb chlorine very readily at the temperature of the decomposition (about 200—240°), hence much of the chlorine first evolved is usually reabsorbed.

When quantities of 1 gram were decomposed at atmospheric pressure in times varying from 15 to 65 minutes, the chlorine given off varied from 45 to 60·6 per cent. of the amount originally present in the chlorate actually decomposed. The employment of a stream of nitrogen increased this proportion, the series of experiments thus carried out pointing to 87·5 per cent. of chlorine as the limiting value when reabsorption is entirely eliminated, although Spring and Prost (*Bull. Soc. Chim.*, 1889, [iii], 1, 340) obtained only 8 per cent. in the decomposition of large quantities. Only 81·4 per cent. could be obtained by reducing the pressure to 2 mm., but this is probably accounted for by the necessary increase of temperature having facilitated reabsorption; it seems remarkable that decrease of pressure should markedly impede the decomposition of the chlorate. Addition of lead chloride appears to have no effect whatever.

In violent decompositions (lasting about 1 second) at atmospheric pressure, some oxychloride was formed, and only about 39 per cent. of the chlorine was obtained. Similar decompositions at pressures varying from 6 to 20 mm. gave 58·5 per cent., but the much higher temperature must no doubt have prevented the reabsorption from being even then successfully eliminated.

The author concludes that the slow decomposition of lead chlorate consists of two independent reactions: (1) $Pb(ClO_3)_2 = PbCl_2 + 3O_2$; (2) $Pb(ClO_3)_2 = PbO_2 + Cl_2 + 2O_2$, the latter having about seven times the velocity of the former. At the same time, the reaction $PbO_2 + Cl_2 = PbCl_2 + O_2$ proceeds to a greater or less extent according to the conditions, and may result in much of the chlorine being reabsorbed. The mechanism in rapid decomposition is probably similar, except that

the higher temperature decomposes much of the peroxide giving oxychloride.

***56. "The bromination of benzeneazophenol." By J. T. Hewitt and W. G. Aston.**

One of the authors recently (*Trans.*, 1900, 77, 99) described the nitration of benzeneazophenol with dilute nitric acid at 40—45°. The production of benzeneazo-*o*-nitrophenol agreed with the formulation of benzeneazophenol as a hydroxylic derivative of azobenzene, but was not compatible with the structure of quinonephenylhydrazone. Shortly after the publication of these results, a note by Professor Armstrong (*Proc.*, 1899, 15, 243) appeared in which it was stated that bromine and benzeneazophenol yielded a product giving *p*-bromoaniline and phenol on reduction. The authors find, however, that the first product of the action of bromine on benzeneazophenol is benzeneazo-*o*-dibromophenol, if the bromination is carried out in acetic acid solution to which sodium acetate is added in order to prevent any formation of quinonephenylhydrazone hydrobromide. In fact, with the exercise of care in the matter of cooling, and the slow addition of the acetic acid solution of bromine, a nearly quantitative yield may be obtained, the substance separating immediately in a very pure condition.

Benzeneazo-*o*-dibromophenol melts at 136° (corr.); it forms a well crystallised sodium salt, but no hydrochloride or hydrate has been obtained, although it gives a sulphate with concentrated sulphuric acid.

The *acetyl* derivative melts at 143°, the *benzoyl* derivative at 120°, and the *ethyl ether* at 71°. The latter compound does not show any mobility of its bromine atoms, boiling for one hour with acetone leaving it unchanged. The substitution of other azophenols is being investigated.

***57. "A new glucoside from willow bark." By H. A. D. Jowett, D.Sc.**

Having had occasion to examine a bark purchased as that of black willow, which could not be further identified than as some species of *Salix*, it was found that the glucoside contained in the bark was not salicin, but a new compound. Chemical examination has shown it to be the glucoside of *m*-oxybenzaldehyde, and the name *salinigrin* is provisionally suggested for it. It is contained in the bark to the extent of about 1 per cent., and is a white, crystalline substance melting at 195° (corr.).

It is soluble in 52·2 parts of water and in 218·2 parts of alcohol at

15°, and is lævorotatory $[\alpha]_D^{15} = -87{\cdot}3°$. From salicin, it is sharply distinguished by yielding a colourless solution with sulphuric acid salicin under similar conditions producing a blood-red colour. Its formula is $C_{13}H_{16}O_7$, and it splits up, on hydrolysis, into *d*-glucose and *m*-oxybenzaldehyde.

***58. "Alkylation by means of dry silver oxide and alkyl iodides." By George Druce Lander, D.Sc.**

In addition to the results given (this vol., 6), the following were described. By the action of dry silver oxide and ethyl iodide on acetanilide, ethyl *i*-acetanilide, $C_6H_5N{:}C(OC_2H_5)CH_3$, is produced. This is a colourless, mobile liquid, boiling at 207—208°, easily hydrolysed by mineral acids into aniline, acetic acid, and alcohol. By warming with aniline, diphenyl ethenyl amidine, $PhN{:}C(NH{\cdot}Ph)CH_3$ (m. p. 131—132°) is formed.

Ethyl malonate, by prolonged boiling with an excess of oxide and ethyl iodide, is partially ethylated, nearly 8 grams of ethyl ethylmalonate being obtained from 32 grams of ethyl malonate.

The action of silver oxide and methyl iodide on salicylic acid gave methyl methoxybenzoate boiling at 245°; the free acid melted at 99°.

Oxidation may also occur, as in the following cases. In alkylating benzoin, part is oxidised to benzaldehyde and benzoic acid, the latter being then alkylated. In the alkylation of ethyl acetoacetate, if the iodide be added to the mixed ethereal salt and oxide, a small quantity of a high boiling oxidation product, probably ethyl diacetylfumarate, is formed which crystallises from ether in fine needles (m. p. 102—105°).

59. "The interaction of mesityl oxide and ethyl sodiomethylmalonate." By Arthur William Crossley.

By the condensation of mesityl oxide with ethyl sodiomethylmalonate, *ethyl trimethyldihydroresorcylate*, $C_{12}H_{18}O_4$, is obtained, which separates from a mixture of chloroform and light petroleum as a microcrystalline powder melting at 94°. On hydrolysis with alcoholic potash, it yields *trimethyldihydroresorcinol*, $(CH_3)_2C\langle^{CHCH_3{\cdot}CO}_{CH_2\text{——}CO}\rangle CH_2$, which crystallises in clusters of needles melting at 99·5—100°. The *ethyl* ether, $C_{11}H_{18}O_2$, is a faintly yellow oil boiling at 264—265° (750 mm.), and the *silver* derivative a white, flocculent precipitate.

By oxidising the resorcinol with sodium hypobromite, it is converted into an acid having the formula $C_8H_{14}O_4$, which melts at

88° and seems to be $\alpha\beta\beta$-trimethylglutaric acid. If the oxidation be arrested before it is complete, a *dibromo-* and a *monobromo*-derivative may be obtained. The former, having the formula $C_9H_{12}Br_2O_2$, crystallises from alcohol in needles melting at 112·5°, and the latter $C_9H_{13}BrO_2$, separates from benzene in glistening plates melting with decomposition at 152°.

The more complete investigation of the properties and reactions of the resorcinol and its derivatives is in progress.

60. "The products of the action of fused potash on dihydroxystearic acid." By Henry Rondel Le Sueur.

From the products resulting from the fusion of dihydroxystearic acid (m. p. 130·5—131°) with potassium hydroxide at a low temperature, two acids have been isolated. One of these is a dibasic acid, $C_{18}H_{34}O_5$, which crystallises from acetic acid in aggregates of long, flat needles melting at 111—111·5°. The *silver* salt, $C_{18}H_{32}O_5Ag_2$, is a white, curdy precipitate, the *calcium* salt crystallises with $3H_2O$, and the *ethyl* salt, $C_{18}H_{32}O_5Et_2$, is a slightly yellow, oily liquid boiling at 269—270° under 30 mm. pressure. The other acid, $C_{18}H_{34}O_3$, crystallises from dilute alcohol in small plates melting at 78·5—79°, and is probably identical with the acid which Saytzeff (*J. pr. Chem.*, 1886, 33, 300) obtained in an impure state by the distillation of dihydroxystearic acid.

If the fusion of the dihydroxystearic acid be carried out at a higher temperature, the main products formed are azelaic acid, pelargonic acid, and an oil which boils at 280—300° under 50 mm. pressure.

The author intends to investigate thoroughly the various products obtained by fusing the dihydroxystearic acids (from oleic and elaidic acids) with alkalis, and to study generally the action of fused alkalis on hydroxylated fatty acids.

ADDITIONS TO THE LIBRARY.

I. Donations.

Bournon, Jacques Louis Comte de. Traité de minéralogie. Première partie, renfermant l'introduction à la minéralogie en général, la théorie de la cristallisation, l'étude de la chaux carbonatée proprement dite, et de l'arragonite, avec application du calcul cristallographique à la détermination des formes cristallines de ces deux substances. Ill. 3 vols. London 1808.

Faraday, Michael. Chemical manipulation, being instructions to

students in chemistry on the methods of performing experiments of demonstration or research with accuracy and success. Ill. Third edition. London 1842.

Fourcroy, Antoine François de. Elements of chemistry and natural history, to which is prefixed the philosophy of chemistry. Fifth edition with notes by John Thomson [W. Nicholson and W. Allen]. Folding plates. 3 vols. Edinburgh 1800.

—— Chemical philosophy, or the established bases of modern chemistry. Translated from the French by W. Desmond. Third edition. London 1807.

Gren, Friedrich Albert Carl. Principles of modern chemistry, systematically arranged. Ill. 2 vols. London 1800.

Griffin, John Joseph. A system of crystallography with its application to mineralogy. Glasgow 1841.

Henry, William. An epitome of chemistry in three parts . . . . Second edition. London 1801.

Lemery, Nicholas. Cours de chemie . . . . Nouvelle édition revuë, corrigée, et augmentée par Theodore Baron. Ill. Paris 1757.

Macquer, Pierre Joseph. A dictionary of chemistry . . . . translated from the French, with plates, notes, and additions by the translator. Ill. 2 vols. in 1. London 1771.

Noad, Henry Minchin. Chemical manipulation and analysis. Part I. Manipulation and qualitative analysis. Part II. Quantitative analysis. Ill. 2 vols. London 1848.

Normandy, Alphonse Réné le Mire. Practical introduction to H. Rose's treatise on chemical analysis, illustrated by synoptic tables and numerous formulas. London 1849.

Pharmaceutical Times, The. A journal of chemistry applied to the arts, agriculture, and manufactures. Vols. I—III. Sept. 5, 1846. Nov. 4, 1848. *continued as*

Chemical Times, The, and Journal of Pharmacy, manufactures, agriculture, and the industrial arts [edited by G. M. Mowbray]. Vol. IV. Nov. 11, 1848—May 5, 1849. London.

Thomson, R. D. A cyclopædia of chemistry, practical and theoretical, with its applications to mineralogy, physiology, and the arts. Ill. London 1854.

Thomson, Thomas. A system of chemistry. Ill. Second edition. 4 vols. Edinburgh 1804.

—— The same. Third edition. 5 vols. Edinburgh 1807.

From the Institute of Chemistry.

A familiar grammar of the principles and practice of chemistry for the use of schools, illustrated by experiments. London 1810.

Bergman, Sir Torbern. An essay on the usefulness of chemistry, and its application to the various occasions of life. London 1783.

Nicholson, William. The first principles of chemistry. Second edition. London 1792.

Rose, Hermann. Chemical tables for the calculation of quantitative analysis. . . . recalculated . . . by William P. Dexter. Boston 1850.

—— A practical treatise of chemical analysis, including tables for calculations in analysis. Translated by A. R. le M. Normandy. London 1848.

Skrimshire, Fenwick. A series of popular chymical essays: containing a variety of instances of the application of chymistry to the arts and manufactures, to the explanation of natural phenomena, and other useful purposes. Vol. I. only. London 1802.

From J. H. Williamson, Esq., through H. E. Brothers, Esq.

Helm, Georg. The principles of mathematical chemistry: the energetics of chemical phenomena. Translated by J. Livingston R. Morgan. New York 1897. From the Translator.

Ladenburg, A. Lectures on the history and development of chemistry since the time of Lavoisier. Translated from the second German edition by Leonard Dobbin. Edinburgh 1900.

From the Author.

Morgan, J. Livingston R. The elements of physical chemistry. New York 1899. From the Author.

—— An outline of the theory of solution and its results: for chemists and electricians. New York 1897. From the Author.

Richter, Victor von. Organic chemistry, or chemistry of the carbon compounds. Edited by R. Anschütz and G. Schroeter. Translated by Edgar F. Smith. 3rd American from 8th German edition. Vol. II. Carbocyclic and heterocyclic series. London 1900.

From the Publishers.

Warington, R. Lectures on some of the physical properties of soil. With frontispiece. Oxford 1900. From the Author.

—— Sulphate of ammonia, its characteristic and practical value as a manure. London 1900. From the Author.

Pamphlet.

Spring, W. La plasticité des corps solides et ses rapports avec la formation des Roches. Bruxelles 1899. From the Author.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE NEXT BALLOT.

The following Candidates have been proposed for election. A ballot will be held on Thursday, May 3rd, 1900.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

Bain, Alexander William,
2, Muswell Rise, Highgate, N.

Tutor and Teacher of Chemistry. Student at Northern Polytechnic Instn., B.A. (Lond. Univ.), Inter. B.Sc. (Lond.). Advanced Stage Cert. Sci. and Art Dept. Pract. and Theor, Inorg. Chem. Desirous of increasing my knowledge of Chemistry.

Jn. H. Allworthy.	H. F. C. Goltz.
J. T. Dunn.	*John Spiller.*
H. T. Sorrell.	*Geo. Chaloner.*
F. Southerden.	*Arthur J. Starey.*

Beringer, Heinrich Rowland,
11, Dolcoath Road, Camborne.

Druggist and Assistant in Chemistry at the Camborne Mining School. In 1882—1883, two years' training in General and Analytical Chemistry in the Laboratory of the Public Analyst for Cornwall. During the last eight years has made steady progress in Mineral Chemistry.

J. Paul de Castro.	John J. Beringer.
John Gill.	*William A. Tilden.*

John C. Umney.

Britten, Frank Curzon, B.A.,
21, Osbaldeston Road, London, N.

Second Master in Peter Symond's School, Winchester (School of Science). Science Master, Thame Grammar School, September, 1895 to December, 1898. First Assistant, Mansfield Technical School, January—July, 1899. Tutor in St. Mark's College, Chelsea, September—December, 1899.

W. W. Fisher.	A. E. Tutton.
A. Vernon Harcourt.	J. E. Marsh.
P. Elford.	C. H. H. Walker.

Brooke, John Richard, A.I.C.,

20, Aberdeen Park, Highbury, N.; also 37, Mincing Lane, E.C.

Analytical Chemist. Over nine years' practical experience in Analytical Chemistry under Professor John Attfield, F.R.S., and Professor Wyndham R. Dunstan, F.R.S., Sec.C.S. Latterly Analyst to the Lonsdale Hæmatite Smelting Co., Ltd., Whitehaven. Now in business on my own account. Have passed the Final Examination (January, 1900) of the Institute of Chemistry for the Associateship.

Wyndham R. Dunstan.	Arthur W. Crossley.
Julian L. Baker.	H. R. Le Sueur.
Bernard Dyer.	*Samuel Hall.*

Chater, Arthur Brand,

65, Queen Street, Brisbane.

Analytical Chemist. Formerly Lecturer in Chemistry at the College of Pharmacy, Brisbane. Member and ex-President of Queensland Pharmacy Board. Examiner to the Board in Chemistry. Have been retained by the Queensland Government as Consulting Chemist in Industrial Matters.

Wm. Martindale.	*Ernest J. Parry.*
John Barclay.	*Fred W. Fletcher.*
Peter MacEwan.	*J. West Knights.*

Cullinan, Nicholas,

Risca, Monmouthshire.

M.D. (Brux.), L.R.C.P., L.R.C.S., L.F.P.S.G., L.M., D.P.H. (Dublin). Six months' Theoretical work, six months' Practical work, and six months' Analytical work for D.P.H.

Geo. R. Thompson.	G. H. Gemmell.
Clarence A. Seyler.	W. Ivison Macadam.
Stevenson Macadam.	Stevenson Macadam, jun.

Cussons, John, B.Sc., A.C.P.,

4, Mount Pleasant, Portmadoc.

Science Master at the County Intermediate School, Portmadoc, Carnarvon. Bachelor of Science (Victoria). Student of Chemistry for four years at the Yorkshire College, Leeds. Since Science Master at the County Intermediate School, Portmadoc.

Arthur Smithells.	Herbert Ingle.
J. B. Cohen.	Thos. Ewan.

Richd. Spencer.

Davis, Arthur Charles,

3, Vinery Road, Cambridge.

Chemist in Chemical Manufactory. Chief Chemist to Messrs.

Keeble Bros., Ltd., and the Saxon Portland Cement Co., Ltd., Cambridge. Late Chemist (now Director) Evison's Chemical Works, Ramsey, Hts. Late Assistant in the Cambridge County Laboratory. Interested in the Chemistry of Cements, Clays, and Agriculture. Contributor of articles on Portland Cement Manufacture to *The British Clayworker*. Desirous of obtaining the Society's publications as an aid to study.

J. West Knights. Austin Keen.
Arthur Deck. William Elborne.

D. B. Butler.

Deerr, Noël Fielding,

26, South Parade, Chelsea, S.W.

Analytical Chemist. Associate of the City and Guilds of London Institute. Resident Chemist at Plantation Albion, Demerara. Author of three papers dealing with the thermal constants of the Elements. *Proc. Chem. Soc.*, June 6th, 1895, *Chemical News* (71, p. 303; 76, p. 224).

Henry E. Armstrong. F. Stanley Kipping.
Gerald T. Moody. G. Harris Morris.

Arthur R. Ling.

Donald, William,

Saltcoats, Ayrshire.

Explosives Chemist. I received my general education at Glasgow from 1862—1873. I studied Chemistry at Glasgow under Dr. Moffat, Dr. Thorpe, and Mr. M. M. Pattison Muir. I was for five years Assistant Chemist to Mr. James Mactear, St. Rollox, Glasgow. Chemist to Nobels, Glasgow, for ten years. Laid out works in Cornwall. Chief Chemist and Works Manager to Explosives Company in South Wales. Inventor of the Chlorine Processes which bear my name. Chemical Engineer to War Office, Turkey. Now Chief Chemist and Works Manager to High Explosives Company, Great Oakley, Essex.

James Mactear. R. T. Thomson.
R. R. Tatlock. *Frank W. Young.*

John S. Lumsden.

Eadie, Robert, jun.,

31, Clarendon Street, Partick, N.B.

Analytical Chemist. Studied Chemistry for three Evening Sessions under Professor A. H. Sexton, F.C.S., F.I.C., at the Glasgow and West of Scotland Technical College; and for ten years Assistant with Dr. C. M. Aikman, F.C.S., F.I.C., in his private laboratory.

C. M. Aikman. R. T. Thomson.
R. R. Tatlock. James Robson.

A. Humboldt Sexton.

Ellis, Frederic Richard,

15, Elton Road, Bishopston, Bristol,

Chemist. Minor Diploma Pharmaceutical Society, Great Britain, 1894. Assistant Diploma Society Apothecaries, London, 1891. Engaged in Manufacturing Chemistry and Analytical Work for Major Diploma of the Pharmaceutical Society, and B.Sc. Degree London University.

Ernest H. Cook. H. W. Jones.
Frank H. Alcock. *Sydney Young.*

W. F. Wyley.

FitzGibbon, Thomas,

1, Clyde Cottages, Ilford, Essex.

Analytical and Manufacturer's Chemist. Late Assistant Chemist at "The London School of Brewing and Chemistry," now Analytical and Manufacturing Chemist to "The Victoria and Royal Albert Docks' Chemical Works.

Theo. D. Lichtenstein. J. T. Hewitt.
F. Jewson. L. W. Mathieson.
D. S. Macnair. Edgar S. Barralet.

F. Southerden.

Fowler, Morris Broad,

30, West Park, Clifton, Bristol.

Chemist and Works Manager. Have studid Chemistry under Prof. R. Meldola, F.R.S., and also under Profs. W. Jago, F.I.C., and A. G. Bloxam. Have taken First Class Intermediate Scientific Lond. Univ. Have patented various improvements in technical processes.

William Jago. Gerald T. Moody.
A. G. Bloxam. *W. A. Lethbridge.*
R. Meldola. *W. A. Davis.*
F. Southerden. *E. C. Jes.*

Halstead, Reginald Gordon,

3, Rathbone Place, Oxford Street, London.

Chemist in the Laboratories of Messrs. Burgoyne, Burbidges and Co., London. Have been a Student of Chemistry for some years and had considerable experience in Analytical Work.

Thos. Farries. Thos. Tyrer.
Theophilus Pitt. H. Wilson Hake.

John Moss.

Haynes, James Herbert,

73, Boynland Avenue, Bishopston, Bristol.

Science Teacher. B.Sc. (Victoria). Studied Chemistry three years at The Owens College, Manchester. Science Teacher, Urmston

Higher Grade School, 1896—1898. Science Master at the Fairfield Higher Grade School, Bristol. Evening Lecturer in Chemistry.

H. B. Dixon. W. H. Perkin, jun.
Wm. A. Bone. G. H. Bailey.
J. F. Thorpe.

Jennings, Henry,

Marlowes, Hemel Hempstead, Herts.

Analyst to London County Council. Student under Prof. Coleman at South Western Polytechnic, Chelsea, from Sept. 1896 to July 1899. Obtained the Associateship of the Institute in Chemistry in 1899. At present time Asst. Chemist, Northern Sewage Outfall, Beckton, Chemical Dept. of the London County Council.

J. Bernard Coleman. *C. J. S. Makin.*
Frank Clowes. *H. F. Fermor.*
R. Grimwood. *E. T. Shelbourn.*

Kershaw, James Henry,

21, Richmond Park Rd., Kingston-on-Thames.

Analytical Chemist. For several years I was a Student under Mr. R. W. Oddy, F.I.C., F.C.S., and Mr. Wm. Marshall, F.I.C., F.C.S., Rochdale. For 6 years I was Assistant to Mr. Oddy, F.I.C., F.C.S., Analytical and Consulting Chemist, Rochdale. At present I am Chemist at Sewage Works, Kingston-on-Thames.

Robt. W. Oddy. T. Mitchell.
William Marshall. *William Dixon.*
Thos. Stenhouse *Walter M. Gardner.*

Liebmann, Adolf,

10, Marsden Street, Manchester.

Ph.D. and M.A. of University of Bonn. For 3 years Assistant of Kekulé. Among papers published: "Synthesis of Cumene"; "Synthesis of the Homologues of Phenol," &c.

James Dewar. W. H. Perkin, jun.
Henry E. Roscoe Alexander Scott.
Henry E. Armstrong.

Lockhart, Thomas Lamb,

Johannesburg, Transvaal.

Analytical Chemist and Assayer. 1889—1893, Assistant Chemist and Assayer, Pollok Gold Extracting Process, Glasgow—California; 1893—1898, Chief Chemist and Assayer, Langlaagte Estate and Gold Mining Co., Ltd., Johannesburg; 1898 to present time, Cyanide Manager and Chemist, Glencairn Main Reef G. M. Co., Ltd., Johannesburg.

Stevenson Macadam. Stevenson Macadam, jun.
W. Ivison Macadam. G. H. Gemmell.
W. S. Anderson.

Macara, Thomas,

6, West Bank Terrace, Hillhead, Glasgow.

City Analyst's Assistant. Student for 3 years with Dr. John Clark, City Analyst, Glasgow. Attended Dr. Clark's Lectures on Chemistry, and Lectures at the Technical College, Glasgow, on Chemistry, Mathematics, Magnetism, and Electricity. Assistant with Dr. Clark for the past 8½ years.

John Clark.	Thomas Gray.
R. R. Tatlock.	*Matthew A. Parker*
R. T. Thomson.	*G. G. Henderson*

Munton, Frederick Thomas,

The Oak House, Winsford, Cheshire.

Analyst to Salt Union. Associate of the Royal School of Mines.

W. C. Roberts-Austen.	W. Palmer Wynne.
William A. Tilden.	W. Gowland.

A. Stansfield.

Pettigrew, Robert,

50, Cresswell Grove, West Didsbury, Manchester.

Analytical Chemist. 3 years Student in Chemistry under the late Professor Dittmar, F.R.S., at the Andersonian College, Glasgow. 2 years Chemist to the London Metallurgical Company. 5 years Assistant Chemist in the laboratory of Sir Henry Roscoe, F.R.S. Silver Medallist of the City and Guilds Institute.

Henry E. Roscoe.	Harry Grimshaw.
Frank Scudder.	Gilbert J. Fowler.

J. Carter Bell.

Phillpotts, Geoffrey Surtees,

82, James Street, Dublin.

Brewing at Guinness's, Dublin. Studied Chemistry for 4 years at Cambridge, taking 1st and 2nd Classes in Parts I. and II. respectively Nat. Sci. Triposes, June, 1898 and 1899. Taught Chemistry at Bedford Grammar School, September to December 1899.

S. Ruhemann.	C. T. Heycock.
H. J. H. Fenton.	F. H. Neville.

T. B. Case.

Sandford, James Wallace,

Adelaide, South Australia, *pro. tem.* c/o Mr. F. J. Lloyd, 4, Lombard Court, London, E.C.

Interested in Chemistry as applied to Agriculture in Australia. Studied Chemistry at St. Peter's College, Adelaide, S. Australia, for 4 years. Also at the Government Agricultural College of South Australia, 18 months. Have been pupil for Chemistry under Mr. F. J.

Lloyd, F.I.C., for 18 months at above address. Have certificates for passing the Junior and Senior Public Examinations, Adelaide University, South Australia.

Fredk. J. Lloyd.	Jas. McCreath.
Alexander Cameron.	*J. H. M. Fallon.*
J. Henry Gilbert.	

Steele, Bertram D., B.Sc. (Victoria),
40, Herndale Road, London, S.W.

1851 Exhibition Research Scholar in the School of Chemistry. Joint Author with Professor Masson of paper "The Blue Salt of Fehling's Solution." Lately *locum tenens* for Professor Rennie at the University of Adelaide.

J. Norman Collie.	William Ramsay.
Arthur Lapworth.	Edward Bevan.
Thomas Tickle.	C. F. Cross.

Tilley, James Walter,
2, Stockwell Crescent, London, S.W.

Consulting and Research Chemist to Messrs. Stevenson and Howell, Ltd, Manufacturing Chemists, Southwark Street, S.E. Have been engaged for 15 years as Laboratory Chemist in connection with Pharmacy and Aërated Water Manufacture. Studied Chemistry and Physics three years at the Birkbeck Institute. Have conducted various researches on Essential Oils with the object of perfecting manufacturing processes.

Reginald Howell.	J. E. Stead.
William Stevenson.	*H. Helbing.*
Charles A. Wrench.	*Peter MacEwan.*

Walker, Augustus John,
3, Arnold Street, Hull.

Science Master. Degree of Bachelor of Science (Vict.). Associate of the Yorkshire College. Five years Lecturer in Theoretical and Practical Chemistry in Day and Evening Science Schools.

Jas. Baynes.	*H. Irving Foster.*
Harry Thompson.	*G. Carr Robinson.*
Frederick William De Velling.	*Alf. J. Parker.*

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Issued 9/5/1900

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 16. No. 223.

May 3rd, 1900. Professor THORPE, F.R.S., President, in the Chair.

A ballot for the Election of Fellows was held, and the following were subsequently declared duly elected :—Messrs. Alexander William Bain, B.A., Heinrich Rowland Beringer, Frank Curzon Britten, B.A., John Richard Brooke, A.I.C., Arthur Brand Chater, Nicholas Cullinan, M.D., John Cussons, B.Sc., Arthur Charles Davis, Noël Fielding Deerr, William Donald, Robert Eadie, Frederic Richard Ellis, Thomas FitzGibbon, Morris Broad Fowler, Reginald Gordon Halstead, James Herbert Haynes, B.Sc., Henry Jennings, James Henry Kershaw, Adolf Liebmann, M.A., PhD., Thomas Lamb Lockhart, Thomas Macara, Frederick Thomas Munton, Robert Pettigrew, Geoffrey Surtees Phillpotts, B.A., James Wallace Sandford, Bertram D. Steele, B.Sc., James Walter Tilley, Augustus John Walker, B.Sc.

Certificates were read for the first time in favour of Messrs. George Edward Battle, Totlands, Dane Park, Ramsgate; John Henry Gough, 22 Francis Street, Chapeltown Road, Leeds; Percy John Hinks, 16 Moreton Road, South Croydon; Tajirô Ichioka, 8 Nottingham Place, London; David Herbert Patrick, Earlsdon, Coventry; Timothy A. Smiddy, Kilbarry House, Cork, Ireland.

Of the following papers, those marked * were read :—

*61. "The substituted nitrogen chlorides and nitrogen bromides derived from ortho- and para-acet-toluide." By F. D. Chattaway and K. J. P. Orton.

Both *o*- and *p*-acet-toluide when treated with hypochlorous or hypobromous acid, produce nitrogen chlorides and bromides which readily undergo transformation into the isomeric substituted toluides; these in their turn form nitrogen chlorides and bromides, which pass into the disubstituted toluides, in which the amino-hydrogen is again replaceable by chlorine or bromine. As with the substituted anilides, when the ortho- and para-positions relatively to the acetamino-group are occupied, the compounds undergo no further isomeric change, hydrolysis or decomposition resulting from attempts to induce it.

The halogen, exactly as in the case of acetanilide or a substituted acetanilide, is found always to take up the para-position when this is possible, and when this position is occupied, the ortho-position, relatively to the carbon to which the nitrogen is attached. The authors have shown (*Trans.*, 1899, 75, 1046; 1900, 77, 134; *Ber.*, 1899, 32, 3573) that substitution by chlorine or bromine in anilines and anilides is not a direct process, but a result of the transformation of a nitrogen chloride or bromide, a hypochlorite or hypobromite being probably formed first by the nitrogen becoming quinquevalent. The behaviour of the nitrogen chlorides and bromides derived from the toluides is in entire agreement with this conclusion.

The properties of the nitrogen chlorides and bromides obtained from the toluides resemble exactly those of other members of the class. The nitrogen chlorides are colourless, the nitrogen bromides sulphur-yellow solids, all crystallising well in four-sided prisms terminated by domes.

All show the general reactions of nitrogen chlorides and bromides. They react with alcohol, re-forming the toluide and producing ethyl hypochlorite or hypobromite, although this action is usually accompanied by a considerable amount of isomeric change.

They react with ammonia liberating nitrogen, with hydrocyanic acid forming cyanogen chloride or bromide, with hydrogen chloride, bromide or iodide setting free the halogen, and with hydrogen peroxide oxygen, in each case the toluide being re-formed. On warming with dilute acids, a certain amount of hydrolysis accompanies the isomeric change, and this, in the case of the nitrogen bromides, is the chief action.

The following compounds are described:

o-*Methyl-phenyl-acetyl-nitrogen chloride* (ortho-acet-chloramino-toluene), $CH_3 \cdot C_6H_4 \cdot NCl \cdot COCH_3$, m. p. 43°.

Methyl-chlor-phenyl-acetyl-nitrogen chloride (ortho-acet-chloramino-5-chlor-toluene), $CH_3 \cdot Cl \cdot C_6H_3 \cdot NCl \cdot COCH_3$ (Me : Cl : : 2 : 4), m. p. 66°.

Methyl-dichlor-phenyl-acetyl-nitrogen chloride (ortho-acet-chloramino-3-5-dichlortoluene), $CH_3 \cdot Cl_2 \cdot C_6H_2 \cdot NCl \cdot COCH_3$ (Me : Cl : Cl : : 2 : 4 : 6), m. p. 78°.

p-*Methyl-phenyl-acetyl-nitrogen chloride* (para-acet-chloramino-toluene), $CH_3 \cdot C_6H_4 \cdot NCl \cdot COCH_3$, m. p. 91—92°.

Methyl-chlor-phenyl acetyl nitrogen chloride (para-acet-chloramino-3-chlor-toluene), $CH_3 \cdot Cl \cdot C_6H_3 \cdot NCl \cdot COCH_3$ (Me : Cl : : 4 : 2), m. p. 48°.

Methyl-dichlor-phenyl-acetyl nitrogen chloride (para-acet-chloramino-3:5-dichlor-toluene), $Cl_2 \cdot CH_3 \cdot C_6H_2 \cdot NCl \cdot COCH_3$ (Me:Cl : Cl : : 4 : 2 : 6), m. p. 72°.

o-*Methyl-phenyl-acetyl nitrogen bromide* (ortho-acet-bromamino-toluene), $CH_3 \cdot C_6H_4 \cdot NBr \cdot COCH_3$, m. p. 100·5°.

Methyl-brom-phenyl-acetyl-nitrogen bromide (ortho-acet-bromamino-5-brom-toluene), $CH_3 \cdot Br \cdot C_6H_3 \cdot NBr \cdot COCH_3$ (Me : Br : : 2 : 4), m. p. 91°.

Methyl-dibrom-phenyl-acetyl-nitrogen bromide (ortho-acet-bromamino-3 : 5-dibromotoluene), $CH_3 \cdot Br_2 \cdot C_6H_2 \cdot NBr \cdot COCH_3$ (Me:Br:Br : : 2:4 : 6), m. p. 120.

p-*Methyl-phenyl-acetyl-nitrogen bromide* (para-acet-bromamino-toluene), $CH_3 \cdot C_6H_4 \cdot NBr \cdot COCH_3$, m. p. 94—95°.

Methyl-brom-phenyl-acetyl-nitrogen bromide (para-acet-bromamino-3-brom-toluene), $Br \cdot CH_3 \cdot C_6H_3 \cdot NBr \cdot COCH_3$ (Me : Br : : 4 : 2), m. p. 87°.

Methyl-dibrom-phenyl-acetyl-nitrogen bromide (para-acet-bromamino-3:5-dibromo-toluene), $Br_2 \cdot CH_3 \cdot C_6H_2 \cdot NBr \cdot COCH_3$ (Me:Br:Br: :4:2:6), m. p. 118°.

***62. "The estimation of hypoiodites and iodates; and the reaction of iodine monochloride with alkalis." By K. J. P. Orton and W. L. Blackman.**

The method of estimating hypoiodites is based on the oxidation of sodium arsenite by hypoiodites, but not by iodates. Excess of the standard arsenite is used, and the unoxidised portion titrated with iodine after the saturation of the alkali by carbon dioxide. The iodate can then be determined by acidifying and titrating the iodine liberated. The hypoiodite solutions were prepared chiefly from iodine monochloride (dissolved in hydrochloric acid), and also from iodine solution. The initial reaction of iodine monochloride and alkalis is represented by the equation $ICl + 2MOH = MIO + MCl + H_2O$.

With potash, soda, lime water, and baryta water, the whole of the iodine is for a short time (varying from 30 seconds to 5 minutes) present as hypoiodite. The transformation into iodate and iodide is practically complete after 24 hours. With ammonia, the complete transformation requires 2 or 3 weeks. The solution obtained from

methylamine and iodine monochloride behaves in an exceptional manner, the hypoiodite gradually disappearing, probably oxidising the methylamine. The bleaching of indigo is shown to be unsuitable for the purpose of estimating hypoiodites, owing to the direct action of even dilute alkalis on the indigo.

The solutions obtained by shaking up iodine with mercuric oxide and water contain chiefly iodate, and only a small quantity of hypoiodite.

DISCUSSION.

In reply to the President, Dr. ORTON said that the work of which he had given an account was completed fifteen months before the abstract of R. L. Taylor's paper (*Proc.*, 1900, **16**, 70) appeared.

***63. "Products of the action of sulphur dioxide on ammonia." By Edward Divers.**

When the paper on "Ammonium amidosulphite" (Divers and Ogawa, *Proc.*, 1900, **16**, 38; *Trans.*, 1900, **77**, 327) was communicated to the Society, the authors were unaware that a paper on the subject of this note had been published by Schumann (*Zeit. anorg. Chem.*, 1900, **23**, 43). Beyond the fact that Schumann also points out the incorrectness of Rose's statement that sulphur dioxide combines with only its own volume of ammonia, the two papers have nothing in common. The main fact established in the paper by Ogawa and the author was the existence of ammonium amidosulphite, of which they had already given notice in a paper on "Ethyl ammoniumsulphite" (*Trans.*, 1899, **75**, 534). Schumann has obtained a product of the same composition as ammonium amidosulphite in red masses, not very hygroscopic, it dissolves in water to a yellow solution, forming ammonium sulphate, sulphite, thiosulphate, trithionate, and pentathionate, whilst ammonium amidosulphite is a white, crystalline powder, extremely deliquescent, and soluble in water, forming ammonium sulphite only. Schumann obtained two other products, having respectively the formulæ SO_2,NH_3 and $3SO_2,4NH_3$, the aqueous solutions of which were similar to that given by the red substance $SO_2,2NH_3$. The author can only regard Schumann's three products as mixtures of substances formed by the spontaneous decomposition of ammonium amidosulphite.

Since the publication of the paper on ammonium amidosulphite, further work by Ogawa has fully established the existence amongst the products of the decomposition of this salt of the compound formulated (*loc. cit.*, p. 334) as $(NH_3)_2S_2O_3$, but of which the true formula is

$N_2H_4S_2O_3$. Although only faintly acid to litmus, it forms salts, of which the *ammonium salt*, $NH_4N_2H_3S_2O_3$, the *potassium salt*, $KN_2H_3S_2O_3$, the *barium salt*, $Ba(N_2H_3S_2O_3)_2,2H_2O$, and the *lead salt*, $Pb(N_2H_3S_2O_3)_2$, have been prepared. The constitutional formula $NH_2{\cdot}S{\cdot}NH{\cdot}SO_3H$, or $NH<\begin{matrix}SO_2\cdot O\\ S\text{—}NH_2\end{matrix}$, seems to express the relations of this substance as far as they are at present known.

This preliminary notice is published because, unfortunately, the circumstances in which the author and Ogawa are placed afford little hope of the full account of the products of the decomposition of ammonium amidosulphite being ready for publication for some considerable time to come.

Discussion.

Dr. Travers asked if the author attributed the formula $NH<\begin{matrix}SO_2\cdot O\\ S\text{—}NH_2\end{matrix}$ to the compound he had described merely from analogy with amidoacetic acid.

Dr. Hewitt asked whether any decomposition products of the compound $N_2H_4S_2O_3$ had been obtained in which the sulphur and nitrogen were still linked together. There seemed to be a possibility of isolating the sulphur analogue of hydroxylamine, or some compound nearly related to it.

Dr. Divers replied that this substance hydrolysed as a sulphonic acid, and yet was not acid to litmus like all other sulphonic acids. The red substance soluble in carbon disulphide and ether might well be the sulphur amide, $S(NH_2)_2$, supposed to exist by Forchhammer.

64. "On Brazilin. IV." By A. W. Gilbody, W. H. Perkin, jun., and J. Yates.

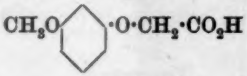
In a previous communication (*Proc.*, 1899, **15**, 27), it was shown that trimethylbrazilin, $OH{\cdot}C_{16}H_{10}O(OCH_3)_3$, when oxidised with chromic acid, is converted into *trimethylbrazilone*, $OH{\cdot}C_{16}H_8O_2(OCH_3)_3$, and that this substance, when heated, loses water, with formation of *dehydrotrimethylbrazilone*, $OH{\cdot}C_{16}H_6O(OCH_3)_3$, a compound which yields an acetyl derivative, and which is evidently identical with the acetyl compound which Herzig prepared by the oxidation of acetyltrimethylbrazilin (*Monatshefte*, 1895, **16**, 913). The authors now find that trimethylbrazilone, on treatment with phenylhydrazine, is reduced to a substance having the formula $C_{19}H_{18}O_4$, which melts at 173°, and dissolves in nitric acid and other concentrated mineral acids, yielding intense purple or orange solutions.

When trimethylbrazilin is oxidised with potassium permanganate

under various conditions, a variety of substances are formed, the principal of which are the following:

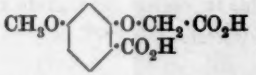
(1.) A dibasic acid, $C_{10}H_{10}O_6$, melting at 175°. This acid contains one methoxyl group, and is derived from the resorcinol portion of the molecule of brazilin, because, when fused with potash, it yields a substance which gives an intense violet coloration with ferric chloride.

When heated with water at 200°, this acid, $C_{10}H_{10}O_6$, is decomposed, with elimination of carbonic anhydride and formation of a monobasic acid, $C_9H_{10}O_4$ (m. p. 119°), which has been shown by synthesis to have the constitution

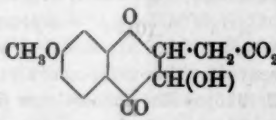


In synthesising this acid, for which the name *methylresorcinolacetic acid* is proposed, pure methylresorcinol, $CH_3O{\cdot}C_6H_4{\cdot}OH$, was treated with sodium ethoxide and ethyl bromacetate, and in this way *ethyl methylresorcinolacetate*, $CH_3O{\cdot}C_6H_4{\cdot}O{\cdot}CH_2{\cdot}CO_2Et$, was obtained as a thick, colourless oil boiling at 182° (25 mm.); this, on hydrolysis, yielded the corresponding acid which melted at 119°, and was found to be identical with the acid $C_9H_{10}O_4$, obtained from brazilin as described above.

Since brazilin under other conditions (see below, and *Proc.*, 1899, 15, 27—29) yields *p*-methoxy-salicylic acid, it follows that the acid, $C_{10}H_{10}O_6$, must be the *methylcarboxyresorcylacetic acid* having the formula



(2.) A monobasic acid, $C_{10}H_8O_3(OCH_3){\cdot}CO_2H$, melting at 129·5°, which has already been described (*Proc.*, 1899, 15, 29). We find that this acid, when treated with concentrated sulphuric acid at 80°, loses water, and is converted into an acid, $C_{12}H_{10}O_5$, which melts at 196°, and when oxidised with permanganate yields *p*-methoxy-salicylic acid. It is therefore probable that the acid, $C_{10}H_8O_3(OCH_3){\cdot}CO_2H$, has the constitution



(3.) An acid very sparingly soluble in water and melting at 208°. This acid has the formula $C_{19}H_{18}O_9$; it yields a *silver* salt, $C_{17}H_{16}O_5(CO_2Ag)_2$, and a *dimethyl* salt, $C_{17}H_{16}O_5(CO_2Me)_2$ (m. p. 110°), and is therefore dibasic. When fused with potash, it yields a substance soluble in

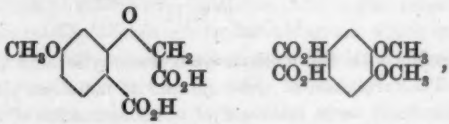
water, which, with ferric chloride, gives an intense catechol reaction; it does not form an oxime, but when reduced with sodium amalgam, it is converted into an acid, $C_{17}H_{16}O_4(CO_2H)_2$, which melts at 227°.

When the acid $C_{17}H_{16}O_5(CO_2H)_2$ is heated at 140° with alcoholic potash, it is decomposed with formation of a neutral substance, the analysis of which agrees better with the formula $C_{17}H_{20}O_5$ than with $C_{17}H_{18}O_5$; it appears probable therefore that, besides elimination of carbonic anhydride, reduction has taken place according to the equation $C_{17}H_{16}O_5(CO_2H)_2 + 2H = C_{17}H_{20}O_5 + 2CO_2$. This substance crystallises from alcohol in needles, melts at 140°, and appears to be a lactone.

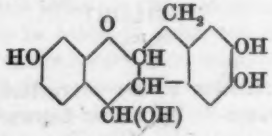
(4.) An acid very sparingly soluble in water, which melts at 214—215° with vigorous decomposition, and gives also an intense catechol reaction after fusion with potash and treatment with ferric chloride. The results of one analysis point to this acid having the formula $C_{18}H_{14}O_8$, but, unfortunately, it has so far been obtained in such small quantity that the analysis could not be repeated.

(5.) Metahemipinic acid.

Constitution of Brazilin.—The results described in this and previous communications, and especially the isolation of methylcarboxyresorcylacetic acid and of metahemipinic acid,



from among the products of the oxidation of brazilin, allow of only a very few formulæ as possible expressions of the constitution of this substance, and after carefully considering all the facts, the authors are of the opinion that brazilin probably has the constitution represented by the formula,



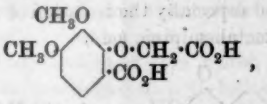
65. "On Hæmatoxylin. V." By W. H. Perkin, jun., and J. Yates.

When *tetramethylhæmatoxylin*, $OH{\cdot}C_{16}H_9O(OCH_3)_4$, is oxidised by potassium permanganate under various conditions, it yields the following substances:

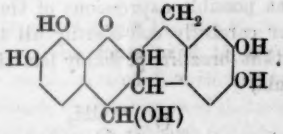
(1.) *Metahemipinic acid*, which was characterised by analysis and by conversion into the characteristic ethylimide melting at 230°. The formation of this acid from tetramethyl-hæmatoxylin by oxidation with chromic acid has already been mentioned (*Proc.*, 1899, 15, 241).

(2.) An acid melting at 180°, which evidently corresponds with the acid $C_{17}H_{16}O_5(CO_2H)_2$ (m. p. 208) obtained from trimethylbrazilin as described in the preceding abstract. This acid has the formula $C_{18}H_{18}O_6(CO_2H)_2$, and is dibasic, since it yields a silver salt $C_{18}H_{18}O_6(CO_2Ag)_2$. It dissolves in concentrated sulphuric acid with a crimson colour, and when reduced with sodium amalgam is converted into an acid, $C_{18}H_{18}O_5(CO_2H)_2$, which melts at 194°.

(3.) An acid melting at 214°, which, when fused with potash, is converted into a substance which with ferric chloride gives the pyrogallol reaction. This acid has the formula $C_{11}H_{12}O_7$, and is dibasic, since its silver salt has the composition $C_{11}H_{10}Ag_2O_7$. It contains two methoxyl groups, and when heated with concentrated hydrochloric acid at 200° it yields pyrogallol. When treated with acetic anhydride, it gives an anhydride, $C_{11}H_{10}O_6$ (m. p. 154°); it therefore has the constitution:



and corresponds with the methylcarboxyresorcylic acid obtained from brazilin. The formation of this acid and of metahemipinic acid from hæmatoxylin leads us to believe that the constitution of this substance is represented by the formula



66. "Note on the function of the characteristic meta-orientating groups." By Arthur Lapworth.

The author desires to draw attention to the following points, the significance of which does not appear to be generally recognised.

The groups ·CO·R, ·NO_2, ·CN, ·SO_2R are known to produce the following effects when in direct attachment to—

(1.) *A benzenoid nucleus.*—They render the hydrogen atom in the *meta*-position directly replaceable by all the characteristic substituting agents, thus differing from all other known groups.

(2.) *A* :CH *group.*—They render the hydrogen atom directly replaceable, and the compounds exist in the tautomeric forms :CH·X:Y and :C:X·YH.

(3.) *A* ·CH_2 *group.*—The compounds are usually capable of condensation with aldehydes, or of entering into the Claisen reaction with esters of oxalic, formic, and nitrous acids in presence of sodium ethoxide, that is to say, under conditions favourable to, if not actually productive of, the "iso"-forms of the compounds in question.

The connection between the foregoing facts is clearly brought out by the use of the mode of analysis suggested by the author (*Trans.*, 1898, 73, 446).

The Claisen reaction is not applicable to nitrobenzene, in which there is no ·CH_2 group, but should, in accordance with the author's view of the function of the above groups when attached to a benzenoid nucleus (*loc. cit.*), be applicable to benzenoid compounds containing a ·CH_2 group in the *ortho-* or *para*-position to one of the groups in question.

Reissert (*Ber.*, 1897, 30, 1030) states that whilst the methyl group of *o-* and *p*-nitrotoluene reacts with ethyl oxalate in presence of alcohol and sodium, no condensation occurs if ethyl nitrite is used. The author finds, however, that reaction occurs if alcohol-free sodium ethoxide and amyl nitrite are employed, and under these conditions *o*-nitrotoluene readily affords *o*-nitrobenzaldoxime, which on hydrolysis and treatment with potash and acetone yields indigo. *p*-Nitrotoluene also reacts, though less readily, with amyl nitrite, affording *p*-nitrobenzaldoxime. If amyl formate be used in these reactions, condensation appears to take place, but the products are more difficult to isolate.

The fact that *m*-nitrotoluene does not react in this respect like the *ortho-* and *para*-compounds is in strict accordance with the author's views. It is hoped that it will be possible to show that the other *meta*-orientating groups behave in the same manner as the nitro-group.

This occasion may be taken to point out that the application of recent views regarding the nature of unsaturated compounds (Thiele, *Annalen*, 1899, 306, 87) to the case of substitution in the benzenoid series appears to lead inevitably to the conclusion, already arrived at by the author (*loc. cit.*), that substitution in the *meta*-position, relatively to one of the above groups, is probably preceded by the formation of a tautomeric compound analogous to the "iso"-forms of the nitro-, cyano-, and keto-paraffins.

ADDITIONS TO THE LIBRARY.

I. Donations.

Cross, C. F., E. J. Bevan, and C. Beadle. La Cellulose. Translated from the English edition of 1895 by R.-G. Lévy and M. Thomas. Paris 1900. From the Authors.

Miller, E. H. The calculations of analytical chemistry. New York 1900. From the Author.

Garçon, Jules. Répertoire général ou dictionnaire méthodique de bibliographie des industries tinctoriales et des industries annexes. Vol. I., premier fascicule. Paris 1900. From the Publishers.

Pamphlets.

Hartley, W. N. On the occurrence of cyanogen compounds in coal-gas, and of the spectrum of cyanogen in that of the oxy-coal-gas flame. (*Proc. Royal Dublin Soc.*, 1900, 9, III.)

Louis, D. A. Notes on gold and platinum mining in the Ural Mountains. (*Proc. Inst. of Mining and Metallurgy*, 1900, vol. viii.).

RESEARCH FUND.

A meeting of the Research Fund Committee will be held in June, Applications for Grants, to be made on forms which can be obtained on application to the Assistant Secretary, must be received on or before May 31st.

At the next meeting, on Thursday, May 17th, the following paper will be communicated by the authors:

"Chlorine derivatives of pyridine. VI. The orientation of some aminochloropyridines." By W. J. Sell, M.A., and F. W. Dootson, M.A.

RICHARD CLAY AND SONS, LIMITED, LONDON AND BUNGAY.

Issued 24/5/1900

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 16. No. 224.

May 17th, 1900. Professor THORPE, F.R.S., President, in the Chair.

Messrs. John R. Brooke, J. Wallace Sandford, and Bertram D. Steele were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Charles Berjew Brooke, Colne House, near Manningtree, Essex; Ernest Owen Courtman, Denford House, Atkin's Road, Clapham Park, S.W.; Henry Bertie Gritton, The Cottage, Balmain, Sydney, N.S.W., Australia; John Beresford Leathes, 10, Park Mansions, Battersea Park, S.W.; Sidney Scrivener Napper, 144, Highbury New Park, N.; Oswald Silberrad, Sunny Croft, Buckhurst Hill, Essex; John Traquair, Glenfield Starch Works, Paisley.

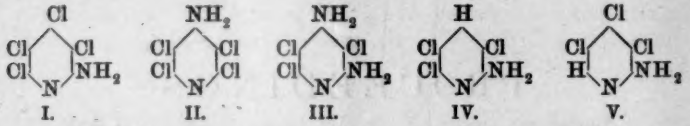
The following Certificates were approved by Council under Bye-law I (3):—Angelo Cantin, Vacoas, Mauritius; M. C. Nanjunda Row, Mylapore, Madras; M. Goolab Roy, Chintadrepettah, Madras.

Of the following papers, those marked * were read:—

***67. "The chlorine derivatives of pyridine. VI. The constitution of some aminochloropyridines." By W. J. Sell, M.A., and F. W. Dootson, M.A.**

The authors gave an account of their work on the constitution of various aminotrichloro- and aminotetrachloro-pyridines which have

recently been described by them. The two compounds, which result from the action of ammonia on pentachloropyridine (*Trans.*, 1898, 73, 777), and which melt at 174—175° and at 212—213°, are shown to have the constitutions represented by the formulæ I and II respectively.



I. II. III. IV. V.

Both compounds heated with ammonia to a higher temperature give the same diaminotrichloropyridine, which must therefore be represented by formula III.

To the aminotrichloropyridine, obtained by the action of ammonia on tetrachloroisonicotinic acid (*Trans.*, 1897, 71, 1083), the constitution represented by formula IV was provisionally assigned (*Trans.*, 1899, 75, 980). This has now been completely established.

The aminotrichloropyridine, obtained (*Trans.*, 1899, 75, 980) by the action of sodium carbonate on a compound containing two pyridine rings, was shown to have the constitution represented by formula V.

***68. "Ortho-substituted nitrogen chlorides and bromides, and the entrance of halogen into the ortho-position in the transformation of nitrogen chlorides." By F. D. Chattaway and K. J. P. Orton.**

When phenylacetyl nitrogen chloride undergoes transformation, a mixture of *o*- and *p*-chloroacetanilide is produced in the proportion of 95—96 per cent. of the latter together with 4—5 per cent. of the former.

The following compounds were described:

Orthochlorophenylacetylnitrogen chloride (acetyl chloramino-2-chlorobenzene), $C_6H_4Cl{\cdot}NCl{\cdot}COCH_3$, colourless, long, flattened prisms, m. p. 88°.

Orthobromophenylacetylnitrogen bromide (acetyl bromamino-2-bromobenzene), $C_6H_4Br{\cdot}NBr{\cdot}COCH_3$, yellow, four-sided prisms, m. p. 150—152°.

Both of these compounds undergo transformation into the 2:4-disubstituted acetanilides.

Discussion.

Dr. Hewitt pointed out that Beilstein and Kurbatow (*Annalen*, 1875, 176, 36) had separated the ortho- from the para-chloraniline by distilling the mixed sulphates with steam, this method being

employed by them on account of the difficulty of isolating pure *o*-chloronitrobenzene from the mixture obtained on nitrating chlorobenzene.

Dr. COLLIE pointed out that if a compound were obtained in which the halogen was attached to a nitrogen atom which was not directly united to the benzene nucleus, it was possible that isomeric change involving the production of a meta-substitution product might result.

***69. "Ammonium imidosulphite." By Edward Divers and Masataka Ogawa.**

The authors have discovered a compound, $3NH_3,2SO_2$, which has the constitution $HN(SO_2NH_4)_2$ and bears the same relation to the amidosulphite as that which exists between imidosulphate and amidosulphate. When ammonim amidosulphite is allowed to decompose completely in a current of well dried hydrogen or nitrogen at a temperature not exceeding 35°, it leaves a coloured residue which is practically insoluble in absolute alcohol. This residue, freely soluble in water, can (with the exception of a small quantity of sulphate) be dissolved by repeated treatments with alcohol of 90 per cent. Rejecting the coloured fractions first obtained, the remainder of the solution on evaporation over sulphuric acid deposits bright, micaceous crystals of the new salt *ammonium imidosulphite*. The mother liquor, which contains much ammonium amidosulphate must be removed by careful washing with 95 per cent. alcohol. The imidosulphite, is very deliquescent and all samples so far prepared have had an acid reaction towards litmus, due to the loss of a little ammonia. By dissolving the ammonium salt in 75 per cent. alcohol and adding exactly the equivalent quantity of alcoholic potash, the pure crystalline *potassium imidosulphite*, slightly alkaline to litmus, is obtained. The imidosulphites react with silver nitrate similarly to the amidosulphites and give with barium chloride a precipitate which readily dissolves in acids, forming a solution which acquires the odour of sulphur dioxide and deposits barium sulphate.

***70. "The constitution of ethyl sodiocyanacetate and of ethyl methylsodiocyanacetate." By Jocelyn Field Thorpe.**

The author pointed out that the reactions of ethyl sodiocyanacetate and of ethyl methylsodiocyanacetate are best represented by the formulæ $CN\cdot CH{:}C(ONa)OEt$ and $CN\cdot C(CH_3){:}C<^{ONa}_{OEt}$ respectively.

When *ethyl sodiocyanacetate* is dissolved in water, the solution is

not alkaline, and on evaporation in a vacuum, leaves sodium cyanacetate. The changes involved may be represented thus:

$$CN\cdot CH{:}C\begin{matrix}ONa\\OEt\end{matrix} + H_2O = CN\cdot CH_2\cdot C\begin{matrix}ONa\\OH\\OEt\end{matrix} = CN\cdot CH_2\cdot CO_2Na + HOEt$$

The production of acid ethyl salts frequently observed in the condensation of ethyl cyanacetate with unsaturated ethyl salts can be thus explained, as the sodium compound of the condensation product, on treatment with water, would yield in a similar way the corresponding sodium ethyl salt. The acid ethyl salts on distillation lose carbon dioxide and pass into the corresponding nitriles.

A number of such condensations were described, and the conditions given under which the maximum quantity of acid ethyl salt is produced. Experiments were described showing that prolonging the time of heating increases the quantity of neutral ethyl salt at the expense of the acid ethyl salt. This is explained by assuming that the first step is the addition of a molecule of alcohol to the unsaturated sodium compound.

Ethyl methylsodiocyanacetate behaves in the same way as ethyl sodiocyanacetate, but its solubility and deliquescent nature render its purification difficult. It condenses with unsaturated ethyl salts to form acid ethyl salts, the yields of which, however, were never more than 17 per cent. of those theoretically possible.

The equation $CN\cdot CHNa\cdot CO_2Et + CH_2{:}CCH_3\cdot CO_2Et = CN\cdot CH(CO_2Et)\cdot CH_2\cdot CNa(CH_3)CO_2Et$, usually supposed to represent a reaction of this kind, is shown to be wrong, because on treating the product of the reaction with methyl iodide, the ethyl salt obtained gives on hydrolysis the symmetrical *aa'*-dimethylglutaric acids, and not the unsymmetrical *aa*-dimethylglutaric acid.

Small quantities of *cis*- and *trans*-acids, such as are obtained from ethyl cyanacetate and ethyl methylcyanacetate, may be separated by the following method. The cyanoethyl salt is converted, by treatment with methyl alcoholic potash into the cyano-acid, which is then boiled with concentrated hydrochloric acid as long as carbon dioxide is evolved. The *cis*- and *trans*-amides, the intermediate products formed, are finally converted, the former into the imide, the latter into the *trans*-acid. The imide is insoluble in dilute sodium carbonate solution, and can thus be separated from the *trans*-acid.

***71. "The $aa_1\beta\beta$-tetramethylglutaric acids." By Jocelyn Field Thorpe and W. J. Young.**

Ethyl sodiocyanacetate, $CN\cdot CH{:}C(ONa)OEt$, separates from absolute alcohol in lustrous plates; with water it gives (see preceding abstract)

sodium cyanacetate; with an ice cold solution of iodine in ether, it reacts to form *ethyl iodocyanacetate*, $CN\cdot CHI\cdot CO_2Et$, a brown oil which decomposes on distillation under diminished pressure; an intermediate addition compound is, however, formed, which reacts with unchanged sodiocyanacetate at higher temperatures to form *ethyl dicyanosuccinate*, thus:

$$CN\cdot CH{:}C\begin{matrix}ONa\\OEt\end{matrix} + CN\cdot CHI\cdot C\begin{matrix}ONa\\I\\OEt\end{matrix} = \begin{matrix}CN\cdot CH\cdot CO_2Et\\CN\cdot CH\cdot CO_2Et\end{matrix} + 2NaI.$$

Ethyl dicyanosuccinate separates from dilute alcohol in glistening plates which melt at 120°.

With bromine dissolved in carbon bisulphide, only *ethyl bromocyanacetate*, $CN\cdot CHBr\cdot CO_2Et$, was obtained as a brownish oil which decomposes on distillation under diminished pressure.

Ethyl methylsodiocyanacetate, $CN\cdot C(CH_3){:}C\begin{matrix}ONa\\OEt\end{matrix}$, is not precipitated on the addition of alcoholic sodium ethoxide to ethyl methylcyanacetate, but is obtained as a gelatinous precipitate on adding an equal volume of dry ether to the solution. It combines with iodine to form *ethyl methyliodocyanacetate*, $CN\cdot C(CH_3)I\cdot CO_2Et$, a brown oil decomposing on distillation under diminished pressure. It condenses with ethyl dimethylacrylate to give the acid salt, $CO_2H\cdot CH(CN)\cdot C(CH_3)_2\cdot CH(CH_3)\cdot CO_2Et$, which, on distillation, loses carbon dioxide and gives *ethyl α-methyl-ββ-dimethyl-γ-cyanobutyrate*, $CN\cdot CH_2\cdot C(CH_3)_2\cdot CH(CH_3)\cdot CO_2Et$, a fairly mobile oil boiling at 224°, which, on hydrolysis, gives *αββ*-trimethylglutaric acid melting at 87°. The preparation of *ethyl α-cyano-aa₁ββ-tetramethyl glutarate*, b. p. 174—176°, and its conversion into *tetramethyl glutarimide* (m. p. 108°), and into trans-*αββα'-tetramethyl glutaric acid* (m. p. 98°) are described. The imide is converted by heating for 2 hours with 50 per cent. sulphuric acid into the *cis*-acid which melts at 140°, and this, on treatment with acetyl chloride yields its anhydride, a liquid boiling at 155—160° (30 mm.). The *cis*-acid is partially converted into the *trans*-acid by heating it in a sealed tube with concentrated hydrochloric acid.

***72. "β-Isopropylglutaric acid, and the *cis*- and *trans*-methyl isopropyl glutaric acids." By F. H. Howles, J. F. Thorpe, and W. Udall.**

The main facts regarding β-isopropylglutaric acid have already been described (*Proc.*, 1899, **15**, 103).

By the action of methyl iodide on the sodium compound of the product resulting from the condensation of ethyl sodiocyanacetate

with ethyl β-isopropylacrylate, *ethyl α-cyano-α-methyl-β-isopropyl glutarate* is obtained as a thick oil boiling at 180—183° (25 mm.). This on hydrolysis with methyl alcoholic potash yields the corresponding *potassium* salt, from the acidified aqueous solution of which the solid cyano-acid may be obtained; this, on boiling with concentrated hydrochloric acid, passes into a mixture of the imide and the *trans*-acid. *α-Methyl-β-isopropyl glutarimide* separates from water in colourless needles melting at 114—115°. Trans-*α-methyl-β-isopropyl glutaric acid* separates from water in microscopic crystals melting at 102°, and is converted into the anhydride of the *cis*-modification on heating with acetic anhydride in a sealed tube.

The *cis*-modification (obtained from the imide by heating with 50 per cent. sulphuric acid) crystallises from water in glistening plates melting at 137°, and on treatment with acetic anhydride is converted into the anhydride which crystallises from light petroleum in prisms melting at 44°.

Ethyl sodiocyanacetate condenses with ethyl α-methyl acrylate to form the acid ethyl salt, $CO_2H{\cdot}CH(CN){\cdot}CH_2{\cdot}CH(CH_3){\cdot}CO_2Et$, which on distillation yields *ethyl α-methyl-γ-cyanobutyrate*, a mobile oil boiling at 205°, giving on hydrolysis α-methylglutaric acid.

By a similar method to that above described *ethyl α-cyano-αα′-dimethylglutarate* (b. p. 181—183°), the *potassium salt* of the cyano-acid, the *cyano-acid* and the cis- and trans-*αα′-dimethylglutaric acids* were prepared.

Ethyl β-methyl-γ-cyanobutyrate and *β-methylglutaric acid* have also been obtained in a similar manner.

***73. "The racemisation of optically active tin compounds. Dextromethylethylpropyl tin dextrobromocamphorsulphonate." By William Jackson Pope and Stanley John Peachey.**

The authors have shown (*Proc.*, 1900, **16**, 42) that the aqueous solution obtained by treating externally compensated methylethyl-*n*-propyl tin iodide with aqueous silver dextrocamphorsulphonate yields only dextromethylethylpropyl tin dextrocamphorsulphonate on evaporation to dryness. They attributed this behaviour to progressive racemisation of the lævorotatory radicle, $(CH_3)(C_2H_5)(C_3H_7)Sn{\cdot}$, attending crystallisation of the sparingly soluble salt of the dextrorotatory radicle. As this, the first well-determined case of the kind recorded, has an important bearing upon the space configuration of quadrivalent sulphur compounds (*Proc.*, 1900, **16**, 12), and upon the preparation of compounds owing their optical activity to the asymmetric nitrogen atom (*Trans.*, 1899, **75**, 1127), it seemed to merit further investigation.

On treating externally compensated methylethyl-*n*-propyl tin iodide

with silver dextro-α-bromocamphorsulphonate in warm aqueous solution and evaporating the filtered liquid, *dextromethylethylpropyl tin dextrobromocamphorsulphonate*, $(CH_3)(C_2H_5)(C_3H_7)Sn(C_{10}H_{14}BrOSO_3)$, separates in colourless plates which, after crystallisation from acetone, melt at 194—197° with previous softening; the mother liquors yield, on evaporation, further deposits of the same salt and no trace of salt of the lævorotatory base could be obtained. The behaviour of the dextrocamphorsulphonate and the dextrobromocamphorsulphonate is thus the same, the whole of the lævorotatory base, $(CH_3)(C_2H_5)(C_3H_7)Sn{\cdot}OH$, becoming converted into its dextrorotatory isomeride. In dilute aqueous solution, the bromocamphorsulphonate has the molecular rotation +318°, which, accepting Walden's value, $[M]_D = +270°$, for the bromocamphorsulphonic acid radicle, allows $[M]_D = +48°$ for the basic radicle; the value, $[M]_D = +45°$, previously obtained from the dextrocamphorsulphonate is thus confirmed.

A crucial test of the truth of the explanation based on progressive racemisation is now possible, for if the intramolecular mobility of the base, $(CH_3)(C_2H_5)(C_3H_7)SnOH$, is such that racemisation can effect total conversion of the externally compensated base into the dextrorotatory component, the reverse should occur under favourable conditions. A one per cent. aqueous solution of the crystalline dextrobromocamphorsulphonate was made in the cold, and the molecular rotation of the dissolved salt was found to be +318°. The solution was then sealed up in a tube and heated on the water-bath for 2 hours; after cooling, the molecular rotation was found to be now only +273°. As the molecular rotation of the acid is +270°, the base must exist wholly racemised in the solution. Some of the solution was then evaporated to dryness on the water-bath, and, after cooling, made up to its original volume by dissolving the residue in cold water; the molecular rotation of the salt in this solution had risen to +315° This experiment was repeated with similar results. Further, the addition of potassium iodide solution to aqueous solutions of dextromethylethylpropyl tin dextrobromocamphorsulphonate before and after heating on the water-bath caused the deposition of dextrorotatory and of optically inactive methylethylpropyl tin iodide respectively.

These facts afford the complete proof that on evaporating externally compensated methylethylpropyl tin hydroxide with either of the optically active acids, the lævo-base is wholly converted into the dextrocomponent by progressive racemisation.

Discussion.

Prof. Percy Frankland called attention to the remarkable mobility of the groups attached to the atom of tin which was quite without

parallel in the case of groups attached to carbon. In no asymmetric carbon compound with which he was acquainted had anything comparable to this facility of racemisation been observed.

74. "Racemic and optically active forms of isoamarine." By H. Lloyd Snape, D.Sc., Ph.D.

The author has examined the behaviour of the isoamarine previously described by Brooke and himself (*Trans.*, 1899, 75, 208) towards nitrous acid, alkyl iodides, acetyl chloride, and nitric acid. Each of these agents acts upon ordinary amarine: and it was desired to contrast the products obtained from the two bases. But, although isoamarine entered readily into reaction in every case, the products were so unstable that as yet the author has failed to prepare them in pure condition.

As the result of further investigation, the anticipation of Japp and Moir (*Trans.*, 1900, 77, 613) that isoamarine is the racemic form of amarine was fully confirmed. Isoamarine, itself optically inactive, was resolved by means of tartaric acid into the acid tartrates, $C_{21}H_{18}N_2 \cdot C_4H_6O_6, 2H_2O$, of the *d*- and *l*-bases, the salt of the *d*-base being much less soluble than that of the *l*-isomeride. From the respective tartrates, the corresponding bases were obtained by precipitation with ammonia. The *l*-base was more difficult to obtain in a state of purity; but it was evident that the optical antipodes had been obtained, the one giving for $[\alpha]_D$ $+62{\cdot}02°$, and the other $-61{\cdot}30°$ to $-58{\cdot}65°$, these values being determined in ethyl acetate solution, after the rotation had become constant.

The racemic base has a higher melting point and density, but a smaller solubility, than the optical antipodes.

Mr. W. J. Pope has kindly measured the crystals of *d*- and *l*-isoamarine, and states that they are orthorhombic prisms, sphenoidally hemihedral, the crystals of the *d*-base showing the form $O\ -k\{111\}$, whilst those of the *l*-isomeride show the form $O\ +k\{111\}$. The crystals of the two substances are thus enantiomorphously related.

The racemic base was synthesised from the *d*- and *l*-isomerides by mixing them in alcoholic solution; but neither of the latter was racemised when heated alone with alcohol to 200°.

ADDITIONS TO THE LIBRARY.

I. Donations.

Richter, V. von. Organic chemistry; or chemistry of the carbon compounds. Edited by R. Anschütz, and translated by E. F. Smith. Third American from the eighth German edition. Volume II. Carbocyclic and heterocyclic series. London 1900.
From the Publishers.

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Lippmann, E. O. von. Die Chemie der Zuckerarten. 2nd ed. Braunschweig 1895.

Lockyer, Sir Norman, K.C.B., F.R.S. Inorganic evolution as studied by spectrum analysis. Ill. London 1900.

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Rupe, Hans. Die Chemie der natürlichen Farbstoffe. Braunschweig 1900.

Süvern, Carl. Die künstliche Seide, ihre Herstellung, Eigenschaften, und Verwendung. Ill. Berlin 1900.

Wiesner, Julius. Die Rohstoffe des Pflanzenreiches. 2nd ed. Parts 1 and 2. Ill. Leipzig 1900.

Bericht über den III. Internationalen Congress für angewandte Chemie, Wien 1898. Drei Bände verfasst von dem Generalsecretär des Congresses Friedrich Strohmer. Wien 1899.

Chemical Review, The. A monthly journal for manufacturing chemists and druggists, dyers, printers, bleachers, sizers, paper makers and stainers, leather dressers, &c. Vols. 7—13. London 1878—85.

Dieterich, Karl. Analyse der Harze-Balsame und Gummiharze nebst ihrer Chemie und Pharmacognosie. Berlin 1900.

Schultz, Gustav. Die Chemie des Steinkohlentheers. Dritte vollständige umgearbeitete Auflage. Erster Band: Die Rohmaterialien. Braunschweig 1900.

RESEARCH FUND.

A meeting of the Research Fund Committee will be held in June, Applications for Grants, to be made on forms which can be obtained on application to the Assistant Secretary, must be received on or before May 31st.

RICHARD CLAY AND SONS, LIMITED, LONDON AND BUNGAY.

Issued 13/6/1900

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 16. **No. 225.**

June 7th, 1900. Professor THORPE, C.B., F.R.S., President, in the Chair.

Messrs. T. G. Joyce, A. W. Bain, T. FitzGibbon, and B. Jordan-Smith were formally admitted Fellows of the Society.

The following certificate was read for the first time:—Edmund Foster Hudson, Churcher's College, Petersfield, Hants.

Professor DUNSTAN, on behalf of the Society, congratulated the President on the distinction recently conferred upon him by Her Majesty.

The PRESIDENT returned his thanks to the Society for their congratulations.

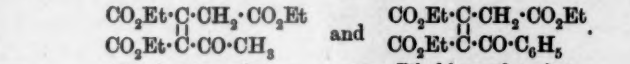
Of the following papers, those marked * were read:—

***75. "Condensation of ethyl acetylenedicarboxylate with bases and β-ketonic esters." By S. Ruhemann and H. E. Stapleton.**

The esters previously obtained (*Trans.*, 1896, 69, 530, 1383; 1897, 71, 323) by the action of ethyl acetoacetate and ethyl benzoylacetate on ethyl chlorofumarate had been formulated thus:

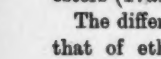
$$\begin{matrix} CO_2Et\cdot C\cdot CH\cdot CO_2Et \\ CO_2Et\cdot CH\cdot CO\cdot CH_3 \end{matrix} \quad \text{and} \quad \begin{matrix} CO_2Et\cdot C{=}CH\cdot CO_2Et \\ CO_2Et\cdot CH\cdot CO\cdot C_6H_5 \end{matrix}.$$

These esters were found by the authors to be identical with those which are formed by using ethyl acetylenedicarboxylate instead of ethyl chlorofumarate (*Trans.*, 1899, **75**, 784). The considerations brought forward (*Trans.*, 1900, **77**, 242) led to the conclusion that these esters should be represented by the formulæ:

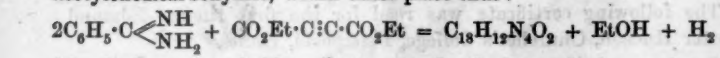


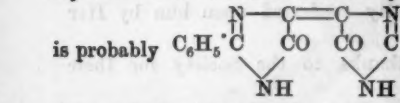
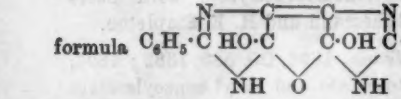
Ethyl acetoaconitate. and Ethyl benzoylaconitate.

The latter expressions are in harmony with the facts that these esters do not give a coloration with ferric chloride and that the same substances are produced by using chlorofumaric and chloromaleic esters (*Trans.*, 1896, **69**, 530).

The difference in the behaviour of ethyl acetylenedicarboxylate from that of ethyl phenylpropiolate is also found in its reactions with guanidine and benzamidine. The former base yields with it a cyclic compound which has both basic and acidic properties, and is regarded by the authors as ethyl amidohydroxypyrimidinecarboxylate,  . This ester, on boiling with potassium hydroxide, hardly undergoes any change beyond hydrolysis to the corresponding acid.

Quite unexpected is the reaction of benzamidine with ethyl acetylenedicarboxylate, which takes place thus:



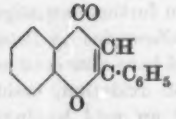
(the hydrogen probably effects a reduction), producing ruby-red crystals of a substance called *glyoxaline red*. Its constitution is probably  , which indicates the close relationship of this compound to indigo and pyrazole blue. Glyoxaline red, when boiled with glacial acetic acid, takes up one molecule of water, and is transformed into a substance, $C_{18}H_{14}N_4O_3$, crystallising in yellow needles, for which the authors suggest the formula  .

This compound dissolves in potassium hydroxide, forming a yellow solution which, gradually acquires the red violet colour of the alkaline solution of glyoxaline red.

The authors have found that the same substances are formed from guanidine as well as from benzamidine by using ethyl chlorofumarate instead of ethyl acetylenedicarboxylate.

*76. "Condensation of phenols with ethyl phenylpropiolate." By S. Ruhemann and F. Beddow.

The ease with which the esters of the acetylene series form additive products induced the authors to study their behaviour towards phenols. They find that the sodium phenoxides readily combine with ethyl phenylpropiolate to form aryl derivatives of ethyl β-hydroxycinnamate; thus in the case of sodium phenoxide itself the following reaction takes place, $C_6H_5\cdot C{:}C\cdot CO_2Et + C_6H_5\cdot OH = \begin{matrix} C_6H_5\cdot C{:}CH\cdot CO_2Et \\ O\cdot C_6H_5 \end{matrix}$. It was hoped that these esters might be converted into flavone and its derivatives, according to the equation:

$$\begin{matrix} C_6H_5\cdot C{:}CH\cdot CO_2Et \\ O\cdot C_6H_5 \end{matrix} = \text{  } + Et\cdot OH,$$

but up to the present this has not been accomplished, because the esters are so easily hydrolysed to the corresponding acids, whilst the acids themselves, on heating, lose carbon dioxide and yield phenoxystyrene, $\begin{matrix} C_6H_5\cdot C{:}CH_2 \\ O\cdot C_6H_5 \end{matrix}$, and its homologues; further, on warming phenoxystyrene with dilute acids, it decomposes into acetophenone and phenol, thus, $\begin{matrix} C_6H_5\cdot C{:}CH_2 \\ O\cdot C_6H_5 \end{matrix} + H_2O = C_6H_5\cdot CO\cdot CH_3 + C_6H_5\cdot OH$. The homologues of phenoxystyrene decompose in a similar manner.

The authors found that ethyl phenylpropiolate reacts with the sodium derivatives of *o*- and *p*-cresol to form compounds analogous to those obtained with sodium phenoxide. The α- and β-naphthols also react in a similar manner with the ester, and form the ethyl esters of the naphthoxycinnamic acids, thus from α-naphthol ethyl α-naphthoxycinnamate and the corresponding acid were prepared; this acid seems to be less stable than those obtained from phenol and the cresols, as it undergoes decomposition when left in contact with dilute sulphuric acid, acetophenone being produced.

*77. "The constitution of pilocarpine." By H. A. D. Jowett, D.Sc

In a recent paper (*Trans.*, 1900, 77, 494), the author gave an account of some preliminary experiments on isopilocarpine, and reserved the

question of the constitution of the alkaloid for a future paper. Owing to the publication of a paper on pilocarpine by Pinner and Kohlhammer (*Ber.*, 1900, 33, 1424), the author has deemed it advisable to give a brief account of the results he has thus far obtained.

Action of Fused Potash on Isopilocarpine.—It was shown (*loc. cit.*) that ammonia, methylamine, and an acid, probably isobutyric, were formed in this reaction. It has now been proved that isobutyric acid is formed, in addition to other acids which are produced in quantity too small to be identified.

Distillation of Pilocarpine with Soda Lime.—A preliminary experiment had shown that the bases formed in this reaction are ammonia and either 2- or 3-methylpyridine. Further investigation has shown that, in addition, methylamine is formed, and that only a very small quantity of 3-methylpyridine is produced. As the formation of traces of a pyridine base by distillation with soda lime, does not throw very much light on the constitution of the alkaloid, this reaction has not been further investigated.

Oxidation of Isopilocarpine by Potassium Permanganate.—The oils previously mentioned have now been examined, and it has been proved that the products of oxidation, besides ammonia and methylamine, are acetic acid and an acid having the formula $C_7H_{10}O_4$. The quantity of permanganate required for the oxidation is about 6 molecular proportions, and the reaction may be expressed by the following equation: $C_{11}H_{16}O_2N_2 + 7O + H_2O = NH_3 + CH_3NH_2 + C_7H_{10}O_4 + 3CO_2$.

The new acid was obtained as the ethyl ester, and the yield was 70 per cent. of the theoretical. The acid is a very slightly coloured, yellow oil, with a peculiar smell, and boils at 210—220° at 10 mm. pressure. By titration, it was shown to be a lactonic acid.

The ethyl ester, $C_9H_{14}O_4$, boils at 299° at atmospheric pressure, is optically active, $[\alpha]_D^{15} = +30{\cdot}76°$, and has a specific gravity 1·1053 (15°/15°).

The ethyl ester reacts with phosphorus pentabromide, yielding the bromethyl ester, which was isolated as an oil boiling at 165—170° (20 mm.). This was treated with diethylaniline, and the unsaturated ethyl ester, boiling at 155° (10 mm.) hydrolysed, when an acid was obtained which boiled at 180—200° (10 mm.), and answered Baeyer's test for an unsaturated acid. It was now oxidised, first with cold permanganate, and then with chromic acid, to an acid which was proved by analysis of the crystalline silver salt to be isobutyric acid.

The probable formula for the lactonic acid is therefore

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH\cdot\underset{\displaystyle O\!-\!CO}{CH}\cdot CH\cdot CO_2H.$$

Action of Methyl Iodide on Isopilocarpine.—When isopilocarpine

methiodide is heated with potash solution in a sealed tube, the base formed is methylamine, thus proving that the nitrogen atom to which pilocarpine owes its basic character is the one eliminated in various reactions as ammonia. By treatment with silver hydroxide and subsequent heating, a new base is formed—*methylisopilocarpine*—which is insoluble in chloroform and forms a crystalline platinichloride, m. p. 218°, and a crystalline picrate, m. p. 136°. This base reacts with methyl iodide to form a methiodide, from which, however, by treatment with silver hydroxide, the original base—methylisopilocarpine—is obtained. It was not found possible to introduce more than one methyl group. Methylisopilocarpine methiodide, on heating with potash solution in a sealed tube, yields only one base—methylamine. These experiments prove the existence of the group :NH in isopilocarpine, and, since the other nitrogen atom always yields methylamine, it must occur as the group $:NCH_3$. Herzig and Meyer have stated that one methyl group is attached to a nitrogen atom, and Chastaing was unable to prepare dialkyl derivatives.

Without proposing any formula for isopilocarpine, it may be desirable to state the facts which any formula for the base must explain:

1. The optical behaviour of pilocarpine and isopilocarpine, and the remarkable stability of the latter base towards heat, alkalis, and various chemical reagents.

2. The non-basic character of the group $:NCH_3$.

3. The existence of the groups $\begin{matrix}CH_3\\CH_2\end{matrix}\!>\!CH\cdot\underset{O}{CH}\cdot\underset{CO}{CH}\cdot CO_2H$,

:NH, and $:NCH_3$.

*78. **"The nitrogen chlorides derivable from meta-chloro-acetanilide and their transformations." By F. D. Chattaway, K. J. P. Orton, and W. H. Hurtley.**

The action of hypochlorous acid on meta-chloro-acetanilide was described. The nitrogen chlorides formed and the transformations they undergo are represented by the following scheme:

$$C_6H_4Cl\cdot N\!<\!\begin{matrix}Cl\\Ac\end{matrix}\left(\begin{matrix}N\ Cl\\1:3\end{matrix}\right)\ \rightarrow\ C_6H_3Cl_2\cdot N\!<\!\begin{matrix}H\\Ac\end{matrix}\left(\begin{matrix}N\ Cl\ Cl\\1:3:4\\\text{and}\ 1:3:6\end{matrix}\right)$$

$$C_6H_3Cl_2\cdot N\!<\!\begin{matrix}Cl\\Ac\end{matrix}\left\{\begin{matrix}N\ Cl\ Cl\\1:3:4\\1:3:6\end{matrix}\right.\!\!\begin{matrix}\rightleftharpoons\\\rightleftharpoons\\\rightleftharpoons\end{matrix}\!\!\left.\begin{matrix}N\ Cl\ Cl\ Cl\\1:2:3:4\\1:3:4:6\\1:2:3:6\end{matrix}\right\}C_6H_3Cl_3\cdot N\!<\!\begin{matrix}H\\Ac\end{matrix}$$

Each of the three tri-chloro-acetanilides yields nitrogen chlorides, which change into the same tetra-chloro-acetanilide (NH : Cl : Cl : Cl : Cl =

1 : 2 : 3 : 4 : 6). In the transformation of these nitrogen chlorides in which one meta-position is occupied, the formation of the ortho-derivatives takes place to a greater extent than in the transformation of the nitrogen chlorides derived from acetanilide (*Proc.*, 1900, **16**, 112). The transformation is also a much slower and more difficult process.

The following substances are described :

Metachlorophenylacetylnitrogen chloride (acetylchloramino-3-chlorobenzene), $C_6H_4Cl\cdot NCl\cdot COCH_3$. Clusters of small prisms, m. p. 93°.

3 : 4-*Dichlorophenylacetylnitrogen chloride* (acetylchloramino-3 : 4-dichlorobenzene), $C_6H_3Cl_2\cdot NCl\cdot COCH_3$. Clusters of very slender prisms, m. p. 92°.

2 : 5-*Dichlorophenylacetylnitrogen chloride* (acetylchloramino-2 : 5-dichlorobenzene), $C_6H_3Cl_2\cdot NCl\cdot COCH_3$. Small prisms, m. p. 73°.

2 : 3 : 4-*Trichlorophenylacetylnitrogen chloride* (acetylchloramino-2 : 3 : 4-trichlorobenzene), $C_6H_2Cl_3\cdot NCl\cdot COCH_3$. Clusters of flattened prisms, m. p. 113—114°.

2 : 4 : 5-*Trichlorophenylacetylnitrogen chloride* (acetylchloramino-2 : 4 : 5-trichlorobenzene), $C_6H_2Cl_3\cdot NCl\cdot COCH_3$. Rosettes of short, thick prisms, m. p. 96°.

2 : 3 : 6-*Trichlorophenylacetylnitrogen chloride* (acetylchloramino-2 : 3 : 6-trichlorobenzene), $C_6H_2Cl_3\cdot NCl\cdot COCH_3$. Small, four-sided prisms or plates, m. p. 116°.

2 : 3 : 4 : 6-*Tetrachlorophenylacetylnitrogen chloride* (acetylchloramino-2 : 3 : 4 : 6-tetrachlorobenzene), $C_6H_2Cl_4\cdot NCl\cdot COCH_3$. Clusters of small prisms, m. p. 97°.

***79. "The persulphuric acids." By T. Martin Lowry, D.Sc., and John H. West.**

This work was undertaken in order to elucidate the part which 'persulphuric acid' plays in the accumulator (Armstrong and Robertson, *Proc. Roy. Soc.*, 1891, **50**, 105) and to ascertain to what extent the production of this acid must be taken into account in discussing the electric conductivity of solutions of sulphuric acid, as well as in determining the origin of the products which such solutions yield when electrolysed under various conditions (Armstrong, *Trans.*, 1895, **67**, 1156).

In the course of the inquiry it became necessary to repeat and extend Berthelot's observations on the interaction of hydrogen peroxide and sulphuric acid (*Ann. Chim. Phys.*, 1878, [v], **14**, 345—354). The experiments have led to results which appear to have an important bearing on the constitution of the product formed by the interaction of sulphuric acid and potassium persulphate, which Caro (*Zeit. angew.*

Chem., 1898, **4**, 845) has shown to be possessed of special properties, and which Bamberger as well as v. Baeyer and Villiger have made use of as an oxidising agent under the name of "Caro's reagent." It has been suggested by v. Baeyer and Villiger that the acid characterised by Caro is a 'persulphuric' acid composed of hydrogen peroxide and sulphuric anhydride in the ratio $H_2O_2 : SO_3$. The authors' experiments favour the conclusion that its composition may be $H_2O_2 : 4SO_3$; the acid of which salts were first prepared by Marshall, being of intermediate composition—$H_2O_2 : 2SO_3$. The members of such a series of persulphuric acids may be provisionally distinguished as 'persulphuric,' 'perdisulphuric' and 'pertetrasulphuric acids.'

Evidence of the composition of the acid in question has been obtained by determining the equilibrium which results on mixing solutions of sulphuric acid and hydrogen peroxide in various proportions. Over fifty different mixtures have been examined, and it has been found that the variation of equilibrium as the concentration changes can be represented by an equation of the type $\frac{c_1}{c_2} = k_1\left(\frac{c_3}{c_4}\right)^2 + k_2\left(\frac{c_3}{c_4}\right)^4$ where c_1 and c_2 are the relative molecular concentrations of the 'persulphuric' acid and hydrogen peroxide, whilst c_3 and c_4 are the relative molecular proportions of sulphuric acid and water in the mixture. The peroxidation is effected almost entirely within the limits H_2SO_4 and $H_2SO_4,5H_2O$. The results indicate that in addition to the 'pertetrasulphuric' acid, a small but increasing proportion of 'perdisulphuric' acid is formed as the concentration decreases, and qualitative tests made in accordance with Caro's directions leave no doubt that this is the case.

80. "On diphenyl- and dialphyl-ethylenediamines, their nitro-derivatives, nitrates, and mercurichlorides." By W. S. Mills, B.A.

When diphenylethylenediamine dissolved in glacial acetic acid is nitrated, a yellow precipitate is obtained towards the completion of the nitration. Purified from nitrobenzene, it melts at 307—308°, and is the *tetranitrodiphenylethylenediamine*, $C_2H_4(NHC_6H_3(NO_2)_2$, of Jedlicka (*J. pr. Chem.*, 1893, [ii], **48**, 202), prepared by the interaction of 2:4-bromodinitrobenzene and ethylenediamine.

Water added to the solution from which the last-mentioned compound has separated precipitates a yellow, amorphous powder very soluble in acetone, ethyl acetate, and acetic acid. It melts at 85°, and is an *isomeric tetranitrodiphenylethylenediamine*, which, when boiled with acetone, is converted into Jedlicka's isomeride.

Diorthotolylethylenediamine nitrated in a similar manner gives a solution from which water precipitates a yellow, amorphous powder,

which melts at 78—79°; it is a *tetranitrodiorthotolylethylenediamine*, $C_2H_4(NHC_6H_2{\cdot}2NO_2{\cdot}CH_3)_2$. When heated with ethyl acetate, this compound undergoes a change similar to that observed in the case of its phenyl homologue, a yellow powder being obtained which melts at 178—180°, and is probably an *isomeric tetranitrodiorthotolylethylenediamine*. Dimetatolylethylenediamine on nitration gives a yellow powder very soluble in acetic acid, melting at 57°, and is *tetranitrometatolylethylenediamine*. Partial nitration of diparatolylethylenediamine gives a mass of fine, orange-red crystals. This is *dinitrodiparatolylethylenediamine*, $C_2H_4(NHC_6H_3{\cdot}NO_2{\cdot}CH_3)_2$, melting at 195—196° and is identical with that prepared by Gattermann and Hager (*Ber.*, 1884, **17**, 778) by the interaction of ethylene dibromide and metanitroparatoluidine.

Diphenylethylenediamine nitrate, $C_2H_4(NHC_6H_5)_2 2HNO_3$, consists of needle-shaped crystals m. p. 164·5°. *Diorthotolylethylenediamine-nitrate*, $C_2H_4(NHC_6H_4CH_3)_2 2HNO_3$, needles, m. p. 152°. *Diparatolylethylenediamine nitrate*, needles, m. p. 166·5°. *Dimetatolylethylenediamine nitrate*, needles, m. p. 153°.

The mercurichlorides are prepared by adding alcoholic solutions of mercuric chloride to alcoholic solutions of the bases in molecular proportions, when crystalline precipitates separate slowly on standing, except in the case of the metatolyl compound, which is obtained by spontaneous evaporation of the mixed solutions. *Diphenylethylenediaminemercurichloride*, $C_2H_4(NHC_6H_5)_2HgCl_2$, well formed rhombic plates, m. p. 129°. *Diorthotolylethylenediamine mercurichloride*, small rhombic plates, m. p. 110°. *Diparatolylethylenediamine mercurichloride*, in white, feathery flakes, m. p. 133°. *Dimetatolylethylenediaminemercurichloride*, rosettes needles, m. p. 79—80°.

81. "Derivatives of cyanocamphor and homocamphoric acid." By Arthur Lapworth.

Cyanocamphor is easily obtained in large quantities by a modification of the method of Bishop, Claisen, and Sinclair (*Annalen*, 1894, **281**, 351). *Chlorocyanocamphor*, $C_8H_{14}\begin{cases}CCl{\cdot}CN\\CO\end{cases}$, crystallises in brilliant prisms melting at 98—100°. Cyanocamphor and its bromo- and chloro-derivatives are dimorphous.

When the halogen derivatives of cyanocamphor are heated with strong aqueous alkalis, reduction occurs, and cyanocamphor and *homocamphoramic acid*, $C_8H_{14}\begin{cases}CH_2{\cdot}CONH_2\\CO_2H\end{cases}$, are produced. The latter crystallises in large prisms which melt and decompose at 209—210°.

Homocamphoric acid crystallises well from nitrobenzene, forming beautiful, white needles which are apparently uniaxial.

When homocamphoric acid is heated with bromine in a sealed tube, action occurs at 140°, but much more than 1 molecular proportion of bromine is used up, and the products are difficult to isolate. When it is brominated in presence of phosphorus pentabromide and the product is treated with alcohol, diethylaniline, and alcoholic potash successively, a *lactone*, $C_{10}H_{16}O_2$, is obtained; this is volatile with steam and crystallises in colourless needles melting at 146°.

α-Bromohomocamphoric acid, $C_8H_{14}\begin{matrix}CHBr\cdot CO_2H\\CO_2H\end{matrix}$, is made by heating the dichloride of homocamphoric acid with bromine on the water-bath. It separates from ethyl acetate in small, six-sided leaflets, and from benzene in slender needles. It melts sharply, under certain conditions, at 181—182°. Unlike all the allied substances, namely, camphoric acid and its halogen derivatives, and homocamphoric acid itself, it dissolves in chloroform and benzene.

When its diethyl ester is heated with diethylaniline, it loses ethyl bromide, and gives the ethyl ester of *homocamphanic acid*,

$$C_8H_{14}\begin{matrix}CH\cdot CO_2H\\ \quad >O\\CO\end{matrix}.$$

The same acid is obtained by warming an aqueous solution of sodium bromohomocamphoric acid; it crystallises in glistening needles or six-sided plates melting at 161—162°.

Experiments are being made with the object of preparing *dehydrohomocamphoric acid*, $C_8H_{13}\begin{matrix}CH\cdot CO_2H\\CO_2H\end{matrix}$, which should afford interesting results on oxidation.

82. "The ultra-violet absorption spectra of some closed chain carbon compounds. II. Dimethylpyrazine, hexamethylene, and tetrahydrobenzene." By W. N. Hartley, F.R.S., and Jas. J. Dobbie, D.Sc., M.A.

It was shown by the authors that dimethylpyrazine, a substance representing a group not hitherto examined spectroscopically, possesses a banded spectrum, the absorption band being both wider and more persistent than that of pyridine. This result was anticipated from the analogy of the constitution of this substance with that of benzene and pyridine. It affords further evidence of the intimate connection between the phenomenon of selective absorption and the benzenoid structure.

The result is further interesting in connection with the question of the constitution of cyanuric acid (*Trans.*, 1882, 41, 48). While pyridine contains the group ·C:N· once in the benzene structure,

dimethylpyrazine contains it twice, and the formula originally proposed for cyanuric acid contains it three times. Accordingly, if this formula were correct for cyanuric acid, we should expect that it would exhibit a powerful absorption band more intense than that of pyrazine. It has, however, been recently shown (Hartley, *Proc.*, 1899, 15, 46) that cyanuric acid has no absorption band.

Specimens of pure hexamethylene and tetrahydrobenzene, prepared by Professor Sydney Young and Miss Fortey, and kindly lent by them, were found to be much more highly diactinic than benzene, and showed no trace of selective absorption. This result confirms the conclusion, previously drawn from the examination of such substances as hexachlorobenzene and piperidine (*Phil. Trans.*, 1885, Part II), that with reduction of the benzene ring the substances are no longer characterised by an absorption band, but by a continuous spectrum indicating a less compact form of linking within the nucleus of the carbon atoms or of the carbon and nitrogen.

83. "A study of the absorption spectra of *o*-oxycarbanil and its alkyl derivatives in relation to tautomerism." By W. N. Hartley, F.R.S., Jas. J. Dobbie, D.Sc., M.A., and Photios G. Paliatseas.

Two ethyl derivatives of *o*-oxycarbanil $C_7H_5NO_2$ are known. One of these is prepared directly from *o*-oxycarbanil by boiling it with equivalent quantities of ethyl iodide and alcoholic potash. This ether is considered to have the lactam constitution, because when heated with hydrochloric acid it takes up water and decomposes into carbon dioxide and the hydrochloride of ethyl-*o*-amido-phenol. The other ether, which is obtained by the interaction of *o*-amido-phenol and ethyl imido-carbonate yields oxycarbanil on treatment with strong hydrochloric acid and is therefore a lactime. The chemical evidence leaves it undecided whether *o*-oxycarbanil itself possesses the lactam or the lactime structure. On photographing the absorption spectra of the three compounds it was found that the spectra of *o*-oxycarbanil are almost identical with those of the lactam ether. The amount of general absorption is practically the same in both cases and the absorption band, which is well marked and persistent, occupies the same position in the spectra of both substances. The spectra of the lactime ether show a smaller amount of general absorption and the absorption band is much less persistent. From the similarity between the spectra of *o*-oxycarbanil and the lactam ether, it is inferred that the parent substance in this case, as in the cases of isatin and carbostyril (*Trans.*, 1899, 75, 640), possesses in solution the ketonic

structure or, if the solution be a mixture of tautomeric modifications, that the ketonic modification predominates almost to the exclusion of the enolic.

84. "Action of formaldehyde on amines of the naphthalene series. II." By G. T. Morgan, D.Sc.

By the action of formaldehyde on ethyl-β-naphthylamine, 2 : 2-*diethyldiamino*-1 : 1-*dinaphthylmethane*, melting at 197—198°, is obtained when the reaction is carried out in cold glacial acetic acid, but when the condensation is effected in hot alcoholic solutions in the presence of hydrogen chloride, it is accompanied by a *compound*, $C_{23}H_{19}NO$ (m. p. 157—158°).

2 : 2-*Dibenzoyldiethyl*-1 : 1-*dinaphthylmethane*, produced from the preceding diamine by the Schotten-Baumann reaction, melts at 196°.

1 : 1-*Tetramethyldiaminodinaphthylmethane*, prepared from dimethyl-α-naphthylamine, melts at 177°; unlike its benzenoid analogue, tetramethyldiaminodiphenylmethane, it does not yield a colour base on treatment with lead peroxide.

Further investigation of the methylene bases derived from 1-bromo-2-naphthylamine and 1-chloro-2-naphthylamine has shown that these substances cannot be formulated on the type $CH_2{:}NR$, as indicated in the preliminary note (*Proc.*, 1899, **15**, 10), but have the constitution indicated by the formula $CH_2(NHR)_2$. They do not combine additively with anhydrous hydrogen cyanide, and when treated with phloroglucinol (Tollen's reagent, *Ber.*, 1899, **32**, 2841), they are quantitatively decomposed, yielding 2 mols. of the parent base and 1 equivalent of methylenephloroglucinol, $(C_7H_6O_3)_x$. It follows from these results that the bromo- and chloro-derivatives must be regarded as *methylenedi*-1-*bromo*-2-*naphthylamine*, $CH_2(NH\cdot C_{10}H_6Br)_2$, and *methylenedi*-1-*chloro*-2-*naphthylamine*, $CH_2(NH\cdot C_{10}H_6Cl)_2$ respectively.

85. "The bromination of benzeneazophenol. II." By J. T. Hewitt and W. G. Aston.

When benzeneazophenol is brominated in a glacial acetic acid solution containing an excess of fused sodium acetate, an almost theoretical quantity of benzeneazoorthodibromophenol is obtained. If, however, the sodium acetate be omitted, a tribromo-derivative is formed having a constitution hitherto unknown. The same product is obtained by bromination in aqueous suspension. This substance has now been proved to be *parabromobenzeneazoorthodibromophenol*. The proof has been furnished by brominating parabromobenzeneazophenol in presence of sodium acetate and benzeneazoorthodibromophenol in presence of

sulphuric acid. The same substance was obtained in both cases, and is identical with that obtained by the direct action of bromine on benzeneazophenol as described above. The corrected melting point of the substance is 148°, and it has been further characterised by conversion into derivatives.

Acetyl ester, m. p. 167°; *benzoyl ester*, m. p. 129°; *ethyl ether*, m. p. 125°.

The isomeric *tribromobenzeneazophenol*, which was prepared from symmetrical tribromaniline for purposes of comparison, and contains the bromine entirely in the benzene nucleus, melts at 168·5°, its *acetyl* derivative at 105°, and its *benzoyl* derivative at 132°.

86. "Condensation of ethyl crotonate with ethyl oxalate." By Arthur Lapworth.

A consideration of the points alluded to in a recent note (*Proc.*, 1900, **16**, 108), made it appear probable that ethyl crotonate and allied compounds would react in presence of sodium ethoxide with esters such as ethyl oxalate, and that substitution would occur, not in the α-position as usual, but in the γ-position, corresponding with the *meta*-position in benzoic acid, and to the position occupied by the hydrogen atoms in the methyl group of *o*- and *p*-nitrotoluene. This has been found to be the case.

Ethyl γ-oxalocrotonate, $EtO_2C{\cdot}CO{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CO_2Et$, is easily prepared from ethyl crotonate and ethyl oxalate by the use of alcohol-free sodium ethoxide. It acts as a fairly strong acid, expelling carbon dioxide from carbonates, and yielding strongly coloured metallic derivatives. Its alcoholic solution is coloured brownish-black by ferric chloride, so that it exists, to some extent at least, in its "enolic" form. It forms nearly colourless crystals melting at 78—80°.

When ethyl γ-oxalocrotonate is hydrolysed by boiling with alkalis it does not give oxalic acid; with hydrochloric acid, *α-pyrone-α'-carboxylic acid*, $CH\begin{cases}CH{=}C{\cdot}CO_2H\\ CH{\cdot}CO\end{cases}>O$, is obtained. This separates from hydrochloric acid in colourless crystals melting at 227—228°.

The formation of ethyl γ-oxalocrotonate in the above manner recalls the observations of Henrich on ethyl glutaconate (*Ber.*, 1898, **31**, 2103), but in the present case the $-CH_2$-group is not united to two unsaturated groups.

There are many facts bearing on "the negative nature of unsaturated groupings" which seem to point to the insufficiency of the view that the hydrogen atom in the grouping $:CH{\cdot}A{:}B$ or $CH<^{A:B}_{C:D}$ is of itself immediately replaceable, and it appears more likely that

the position of attack is usually at a double linkage (compare Henrich, *Ber.*, 1900, **33**, 1437). In the above case, as in many similar ones, it appears not improbable that an intermediate compound derived from a tautomeric form, $\cdot CH{:}CH\cdot CH{:}C\begin{matrix}OEt\\OH\end{matrix}$, is produced, and that subsequently either by addition or isomeric change or by both the γ-carbon atom becomes united with the substituting group (*Trans.* 1898, **73**, 446).

The author proposes to extend the above observations and to examine the capability of other $a\beta$-unsaturated esters of taking part in this and similar condensations.

87. "Researches in silicon compounds. VI. On silicodiphenyldiimide and silicotriphenylguanidine." By J. Emerson Reynolds, Sc.D., M.D., F.R.S.

The author has already described (*Trans.*, 1889, **55**, 474) the well defined crystalline silicophenylamide, $Si(NHC_6H_5)_4$, the first of a new class of compounds in which silicon is exclusively united to nitrogen. It was there stated that when this compound was heated in a vacuum to its melting point (137°) some aniline was given off and a mixture of silicon compounds formed, the constituents of which would be described later. The nature of these products was stated shortly afterwards to the British Association in 1893, but no details were then given. These are now described, before an account of more recent investigations is presented to the Society.

The primary interest attached to the examination of the changes effected by heating silicophenylamide is due to the probable production of silicon analogues of cyanogen compounds.

The study of the action of heat revealed the formation of the *diimide*, $Si(NPh)_2$, which exists in two modifications, one insoluble in benzene and the other soluble, but precipitated by ligroin in droplets which slowly change to the insoluble form. *Silicotriphenylguanidine*, $SiNC_6H_5(NHC_6H_5)_2$, was isolated from the earlier products of the action of heat in small, short rhombic prisms, soluble in benzene. Like all other organic silicon compounds of this kind, it is decomposed by acids, as well as by water and alcohol.

The continued action of heat on the diimide gave rise to a compound represented by the formula $Si_2(NC_6H_5)_3$; this withstood a high temperature without charring, and when heated in dry ammonia left a residue which approximated in composition to $Si_2(NH)_2NC_6H_5$, but the decomposition could not be carried beyond this point without the separation of carbon.

88. "Note on Bach's hydrogen tetroxide." By Henry E. Armstrong.

It is contended by A. Bach (*Ber.*, 1900, **33**, 1506), that the liquid obtained on mixing a solution of hydrogen peroxide with sulphuric acid probably contains hydrogen tetroxide. He bases this conclusion on the observation that when the amount of permanganate which the solution decolorises is contrasted with the amount of oxygen which is evolved, the latter is largely in excess of that which would be obtained if only hydrogen peroxide were present. Bach has obviously failed to take into account the existence of persulphuric acid in such a solution.

In all his experiments—both in those in which palladium hydrogen was oxidised and in those with peroxides—a large excess of normal sulphuric acid was added; the solution was then titrated with permanganate, and the oxygen which was given off was collected and measured. It is noteworthy that the liquid was shaken during several minutes (5—8) after the titration was completed in order to expel the gas. It is open to question whether, in these cases, some persulphuric acid was not formed (Lowry and West, p. 126) by peroxidation of the sulphuric acid, and whether the extra oxygen obtained by Bach was not derived from this.

Bach regards the fact that other dehydrating agents besides sulphuric acid—for example, hydrogen chloride—produce effects, when mixed with hydrogen peroxide, similar to those obtained on using Caro's reagent, as evidence in favour of the view that hydrogen peroxide is converted into tetroxide by dehydration: $3H_2O_2 = H_2O_4 + 2H_2O$. It may be pointed out, however, that the effects produced by Caro's reagent are merely such as it might be anticipated would be exercised by hydrogen peroxide acting in presence of a powerful dehydrating and hydrolysing agent, and it is the use of hydrogen peroxide under such conditions that characterises the novelty in procedure. It is not necessary to assume the existence of any novel specific agent in order to explain them. Caro's original observations stand on a different plane, as they served to establish a difference between the perdisulphates and salts of another acid, and for the first time made it possible to differentiate the acid products of the electrolysis of sulphuric acid.

ADDITIONS TO THE LIBRARY.

I. Donation.

Mendeléeff, D. Recherches expérimentales sur les oscillations de la balance. Translated from the Russian by Mlle. O. Ozarowsky. St. Petersburg 1900. From the Author.

II. By Purchase.

Dugast, J. Vinification dans les pays chauds, Algérie et Tunisie. Paris 1900.

Freind, John. Chymical lectures: in which almost all the operations of chymistry are reduced to their true principles and the laws of nature: read in the Museum at Oxford, 1704. Englished by J. M. 2nd ed. London 1729.

Hjelt, Edvard. Aus Jac. Berzelius' und Gustav Magnus' Briefwechsel in den Jahren, 1828—1847. Herausgegeben von E. H. Braunschweig 1900.

Kunkel, J. Utiles observationes sive animadversiones de salibus fixis et volatilibus, auro et argento potabili, spiritu mundi, et similibus. Item de colore et odore metallorum, mineralium, aliarumque rerum quae a terra producuntur. Trans. from German by C. A. Ramsay. (Dedicated to the Royal Society, with a list of members, 1677). *Also*

Kunkel, J. Observationes chymicae, in quibus agitur de principiis chymicis, salibus acidis et alcalibus, fixis et volatilibus, &c., &c., cum appendice, perspicilli chymici contra non-entia chymica: propria experientia conscriptae. Trans. from German by C. A. Ramsay. London and Rotterdam 1678.

Schmidt, Julius. Uber die Erforschung der Konstitution und die Versuche zur Synthese wichtiger Pflanzenalkaloide. Stuttgart 1900.

Traube, Morris. Gesammelte Abhandlungen. Berlin 1899.

Villiers, A., and Collin, E. Traité des altérations et falsifications des substances alimentaires. Ill. Paris 1900.

Wiesner, Julius. Die Rohstoffe des Pflanzenreiches. 2nd ed. Part 3. Leipzig 1900.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE NEXT BALLOT.

The following Candidates have been proposed for election. A ballot will be held on Thursday, June 21st, 1900.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

Ashton, James,

Sand Hill House, Hoscar Moss, Ormskirk, Lancs.

Manager of the Wigan Sewage Disposal Works and Farm, Resident Chemist at the works, &c. I am Member of the Institute Sanitary Engineers. Author of "Treatment of the Sewage of Wigan," and other papers on sewage purification. Member Society of Chemical Industry.

W. B. Bottomley. Wm. Jas. Orsman.
Wm. Naylor. *John M. Thomson.*
Patrick H. Kirkaldy.

Battle, George Edward,

"Totlands," Dane Park, Ramsgate.

Assistant Master on the staff of the South Eastern College, Ramsgate. 1. Practical Chemistry course in the Dublin University Laboratories under Professor J. Emerson Reynolds, M.D., D.Sc., F.R.S. 2. B.A. of Trinity College, Dublin, with Honours (Junior Moderator) in Experimental Science. 3. Science Master at the South Eastern College, Ramsgate, during the past three years.

J. Emerson Reynolds. George R. Tweedie.
Emil A. Werner. Francis Jones.
William Briggs.

Brooke, Charles Berjen, jun.,

Colne House, Brantham, near Manningtree, Essex.

Manager of the Brantham Works of the British Xylonite Company, Ld. For some time pupil and assistant to Mr. Edward Riley;

since then and at present time Chemist and Manager to the British Xylonite Co., Ld.

J. N. Goldsmith. Wyndham R. Dunstan.
Edw. Riley. *Julian L. Baker.*
John R. Brooke. *Thomas H. Pope.*

Courtman, Ernest Owen,

Denford House, Atkin's Road, Clapham Park, S.W.

Demonstrator in Assaying in the Metallurgical Division, Royal School of Mines. Associate of the Royal School of Mines in Metallurgy and Mining. Have taught for one year in the Metallurgical and Mining Divisions, Royal School of Mines.

W. C. Roberts Austen. William A. Tilden.
W. Gowland. W. Palmer Wynne.
Alfred Stansfield.

Gompertz, Richard Henry Cyril,

110, Elgin Crescent, Notting Hill, W.

Junior Demonstrator in the Chemical Laboratory of the Pharmaceutical Society of Great Britain under Prof. Collie. Student at King's College, London, during the Sessions 1894—1898. Junior and Senior Clothworkers' Scholar, 1894—1897. Appointed Assistant at the Pharmaceutical Society, 1899. B.Sc. London, 1899.

John M. Thomson. Herbert Jackson.
J. Norman Collie. Patrick H. Kirkaldy.
Arthur Lapworth.

Gough, John Henry,

22, Francis Street, Chapeltown Road, Leeds.

Teacher of Pharmacy, Victoria University, Leeds. Pharmaceutical Chemist. Teacher of Pharmacy, Medical Department, Yorkshire College (Victoria University), Leeds. Honours Certificate Chemistry, South London School of Pharmacy.

Thomas Fairley. Harry W. Dixon.
F. W. Branson. *M. Carteighe.*
B. A. Burrell.

Gritton, Henry Bertie,

"The Cottage," Balmain, Sydney, N.S.W., Australia.

Assayer. Was a Student in Chemistry at Sydney University, and afterwards Junior Demonstrator in Chemistry there, and is at present Assistant Assayer at Sydney Branch of The Royal Mint.

A. Liversidge. F. B. Guthrie.
J. A. Schofield. *William M. Hamlet.*
C. Walker. *John C. H. Mingaye.*

Hinks, Percy John,

16, Moreton Road, South Croydon.

Technical Chemist. Associate of The Royal College of Science (London). Associate of the Institute of Chemistry. Formerly Chemist to the British Non-Flammable Wood Co. At present Assistant to Messrs. Cross and Bevan.

William A. Tilden.	G. T. Morgan.
W. Palmer Wynne.	C. F. Cross.
M. O. Forster.	Edward Bevan.

Ichioka, Tajiro,

8, Nottingham Place, London.

Chemist to Japanese Navy (Kaigun-gishi). Graduated Tokio University (Chemical Department), 1889; became Professor of Chemistry to Naval College (Japanese Navy), 1892; and then, in 1897, became Chief Chemist to Imp. Jap. Arsenal at Kure.

Henry de Mosenthal.	Boverton Redwood.
Oscar Guttmann.	Edward Divers.
Otto Hehner.	*B. E. R. Newlands.*

Arthur R. Ling.

Leathes, John Beresford,

10, Park Mansions, Battersea Park, S.W.

Lecturer on Physiology, St. Thomas's Hospital. "Beiträge zur Chemie der Ovarialmucoide," *Archiv. für Exp. Path. und Pharmakol*, 1899. Papers in *Journal of Physiology*, 1895 and 1896. George Henry Lewes Student, 1897—1899. M.A., M.B., Oxon.

Charles E. Groves.	W. D. Halliburton.
Thos. Stevenson.	A. Croft Hill.

Wyndham R. Dunstan.

McKenzie, Alexander Ernest,

11, Bank Road, Workington.

Analytical Chemist (Chief) at C. Cammell and Co.'s, Derwent Works, Workington. Teacher of the South Kensington Science and Art Department's Classes in Chemistry at Workington, 1885—1898. Chief Chemist at C. Cammell and Co.'s Derwent Iron and Steel Works, Workington.

Robert Hellon.	W. H. Pearson.
Archd. Kitchin.	*William Harrington.*

Robt. Carruthers.

McNair, Hugh,

Bellfield, Wishan.

Gas Engineer. Have attended Chemistry Classes in the Glasgow

and West of Scotland Technical College, and wish to keep in touch with the progress of Chemistry through the medium of the Journal of the Society.

Thomas Gray. G. G. Henderson.
Matthew A. Parker. *James Robson.*
John Clark.

Napper, Sidney Scrivener,
144, Highbury New Park, N.

Student at Central Technical College since 1896, taking Diploma in Applied Chemisty in 1899. Now engaged in Research under Professor Armstrong.

Henry E. Armstrong. T. M. Lowry.
Gerald T. Moody. Edward W. Lewis.
William A. Davis. Edwin C. Jee.

Patrick, David Herbert,
Earlsdon, Coventry.

Lecturer in Chemistry and Physics, Bablake School of Science, Coventry. Obtained the Prize for Analytical Chemistry at the Birmingham Municipal Technical School, 1892. Late Teacher of Chemistry at the Coventry Municipal Technical Institute. For the last five years Principal Teacher of Chemistry, Physical and Analytical, at the Bablake School of Science.

W. F. Wyley. H. S. Shorthouse.
H. W. Jones. *Chas. Baylies.*
W. Waters Butler.

Silberrard, Oswald, Ph.D.,
Sunny Croft, Buckhurst Hill, Essex.

Research at the Davy-Faraday Research Laboratory. *Past Experience.*—Certificated Student of Finsbury Technical College. Dr. Phil. University of Würzburg. Worker in Davy-Faraday Laboratory. *Contributions to Chem. Science.*—I. "Über die Polymerisationsproducte aus Diazoessigester," with Prof. Hantzsch (*Ber.*, 33, 58). II. "Synthesis of αα-diglutaric acid," with Prof. Easterfield (University Laboratory, Cambridge), shortly to be published. Work on Tetrazolines in progress.

R. Meldola. Bertram H. Dowles.
Alexander Scott. J. T. Hewitt.
F. Southerden.

Smiddy, Timothy A.,
Kilbarry House, Cork, Ireland.

Soap-manufacturing at Soap Works of W. Smiddy and Son, Cork.

After spending two years at Queen's College, Cork, as Chemical Student, I studied under W. L. Gadd, of Manchester Laboratory, with a view to act as Chemist and Manufacturer in above works, which position I now hold.

Augustus E. Dixon. Patrick J. D. Fielding.
Robert Elliott Doran. Daniel J. Mahony.
P. T. O'Sullivan.

Smith, Herbert Procter,
60, Stepney Street, Llanelly.

Metallurgical Chemist. 1893—95 Senior Demonstrator, Leeds School of Science, under the late Mr. S. J. Harris, M.Sc., F.C.S. 1896—97 Pupil Assistant with Mr. Edward Riley, F.I.C., F.C.S., 2, City Road, E.C. 1897—98 Chief Assistant in Laboratory, Ebbw Vale Coal, Iron, and Steel Co., Ltd., under Mr. F. W. Daw, A.R.C.S., F.I.C., F.C.S. 1898—99 Chief Assistant in Laboratory Sir W. G. Armstrong, Whitworth and Co., Manchester. 1899 Chemist and Manager Alloys Syndicate, Ltd., Llanelly.

Edw. Riley. James E. Ferguson.
F. W. Daw. Robt. D. Connell.
John Allan.

Tomlins, George Edward,
4, Radford Road, Hither Green, London, S.E.

Analyst. Two years as Student of Chemistry at Royal College of Science. Two years' experience as Assistant Analyst in the Government Laboratory.

T. E. Thorpe. William A. Tilden.
E. Grant Hooper. W. Palmer Wynne.
Chapman Jones.

Traquair, John,
Glenfield Starch Works, Paisley, N.B.

Analytical Chemist. Two years a student at City Analyst's Laboratory, Glasgow. Four sessions Evening Classes in Chemistry, Glasgow Technical College. Two years Work's Chemist with F. Henshelwood and Co., Glasgow Oil and Colour Works. Two years Chemist with Wm. Wotherspoon, Glenfield Starch Works, Paisley.

R. R. Tatlock. James McLeod.
R. T. Thomson. C. F. Cross.
G. G. Henderson. *John Clark.*
James Robson. *Horatio Ballantyne.*
Matthew A. Parker. *Edward Bevan.*

The following Certificates were authorised by the Council under Bye-law I (3) :—

Cantin, Angélo,
Vacoas, Mauritius.

Acting Professor of Chemistry, Royal College Mauritius. Undergraduate of the University of London. Has been a successful teacher of Chemistry for the last 11 years at the Royal College of Mauritius, where the students read for the English Scholarship Examination, for the Matriculation Examination of the University of London, and for the Junior and Senior Cambridge Locals.

W. T. A. Edwards.

Row, M. C. Nanjunda,
Mylapore, Madras, South India.

First Assistant Chemical Examiner. B.A., M.B., and C.M. of the Madras University. Assistant Examiner in Chemistry to the University of Madras for the years 1897 and 1898. Assistant to the Professor of Hygiene, Madras Medical College, from March, 1892, to July, 1895, and have been First Assistant to the Chemical Examiner to Government of Madras from July, 1895, which appointment I still hold. In the former appointment, I had opportunities of assisting in the conduct of class work in Practical Hygiene, and in the latter, of carrying out chemical analyses of miscellaneous articles of foods and drugs, and of assisting in the analyses of chemico-legal cases.

J. L. van Geyzel. Samuel Jackson.
J. Walter Leather.

Roy, M. Goolab,
Chintadrepettah, Madras.

Second Assistant to the Chemical Examiner. Have been an Assistant in the Laboratory of the Chemical Examiner to the Madras Government for 17 years, during which period I have had opportunities of conducting a large number of analyses of miscellaneous articles, food, drugs, oils, and explosives. Latterly, I have also assisted in chemico-legal analyses.

J. L. van Geyzel. Samuel Jackson.
J. Walter Leather.

At the next meeting, on June 21st, there will be a Ballot for the Election of Fellows, and the following papers will be communicated :—

"Notes on the chemistry of chlorophyll." By Leon Marchlewski, PhD., and C. A. Schunck.

"Researches on morphine. I." By S. B. Schryver and F. H. Lees.

"A new series of pentamethylene derivatives. I." By W. H. Perkin, jun., J. F. Thorpe, and C. W. Walker.

"Experiments on the synthesis of camphoric acid. III. The action of sodium and methyl iodide on ethyl dimethylbutanetricarboxylate." By W. H. Perkin, jun., and J. F. Thorpe.

"On the oxime of mesoxamide and some allied compounds." By (Miss) M. A. Whiteley, B.Sc.

"The oxyphenoxy- and phenyleneoxy-acetic acids." By W. Carter and Dr. W. T. Lawrence, B.A., Ph.D.

"The condensation of ethyl α-bromo-isobutyrate with ethyl malonates and ethyl cyanacetates: α-methyl-α'-isobutylglutaric acid." By Dr. W. T. Lawrence, B.A., Ph.D.

"Methylisoamylsuccinic acid. II." By Dr. W. T. Lawrence, B.A., Ph.D.

RICHARD CLAY AND SONS, LIMITED, LONDON AND BUNGAY.

Issued 29/6/1900

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 16. No. 226.

June 21st, 1900. Professor THORPE, C.B., F.R.S., President, in the Chair.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—Messrs. James Ashton; George E. Battle, B.A.; Charles Berjen Brooke, jun.; Angélo Cantin; Ernest Owen Courtman; Richard H. C. Gompertz, B.Sc.; John Henry Gough; Henry Bertie Gritton; Percy John Hinks; Tajiro Ichioka; John B. Leathes, M.A., M.B.; Alexander Ernest McKenzie; Hugh McNair; Sidney Scrivener Napper; David Herbert Patrick; M. C. Nanjunda Row, B.A., M.B.; M. Goolab Roy; Oswald Silberrad, Ph.D.; Timothy A. Smiddy; Herbert Procter Smith; George Edward Tomlins; John Traquair.

Of the following papers, those marked * were read:—

***89. "Researches on morphine. I." By S. B. Schryver and F. H. Lees.**

The authors have found that the alcoholic hydroxyl group in morphine is readily replaceable, and they have prepared the compounds described below.

Chloromorphide, $C_{17}H_{18}O_2NCl$, prepared by the action of phosphorus trichloride on dry morphine. It melts at 190° with decomposition, and dissolves readily in chloroform and in methyl alcohol. The *hydrochloride*, $C_{17}H_{18}O_2NCl,HCl$, and *hydrobromide*, $C_{17}H_{18}O_2NCl,HBr$, have also been prepared. On treatment with acetic anhydride, the *monoacetyl* derivative, $C_{17}H_{17}O(OC_2H_3O)NCl$, is obtained melting at 178—179°.

Bromomorphide, $C_{17}H_{18}O_2NBr$, melting with decomposition at 170°, has a very bitter taste and dissolves readily in chloroform and benzene. Its *hydrochloride* and *hydrobromide* crystallise with one molecule of water. Bromomorphide can also be prepared by the action of concentrated hydrobromic acid on morphine.

By treating chloromorphide with tin and hydrochloric acid, *desoxymorphine hydrochloride*, $2(C_{17}H_{19}O_2NHCl),3H_2O$, is obtained as glistening needles. The salt is lævorotatory; $[\alpha]_D^{27} = -140{\cdot}3°$.

It was found that on heating chloro- and bromo-morphide and their hydrochlorides with water, decomposition took place, bromomorphide giving the hydrobromide of a base isomeric with morphine; for this new base the authors propose the name *isomorphine*. Isomorphine and its derivatives are more powerfully lævorotatory than morphine and its corresponding derivatives. The salts of isomorphine are much more readily soluble than those of morphine. Isomorphine melts at 246—247°, is readily soluble in methyl alcohol, but only very sparingly so in ether, chloroform, or benzene. Recrystallised from hot water, it is obtained as glistening needles. In methyl alcohol, $[\alpha]_D^{25} = -164{\cdot}3°$. For the *hydrochloride*, $C_{17}H_{19}O_3N,HCl$, $[\alpha]_D^{25°} = -150°$; for the *hydrobromide*, $C_{17}H_{19}O_3N,HBr,H_2O$, $[\alpha]_D^{20} = -127{\cdot}2°$ for the anhydrous salt. The *methiodide*, $C_{17}H_{19}O_3N,CH_3I$, melts with vigorous decomposition at 279°; in aqueous solution, $[\alpha]_D^{25} = -91{\cdot}5°$. Morphine methiodide also melts at 279°, but for it $[\alpha]_D = -72{\cdot}9°$.

By treatment of isomorphine methiodide in aqueous solution with silver sulphate and barium hydroxide, a very alkaline solution of the hydroxide is obtained, which, dried in a vacuum, sets first to a deliquescent mass of fern-like crystals, and on further dehydration in a vacuum yields a solid which can readily be powdered. This substance dissolved in methyl alcohol does not react in the cold with methyl iodide, but does so readily on warming, giving a methiodide extremely soluble in water and in methyl alcohol, but only slightly so in ethyl alcohol. For it $[\alpha]_D^{25} = -96{\cdot}4°$. This compound is not identical with codeine methiodide.

The determinations recorded in the following table were made with the free bases dissolved in methyl alcohol, and the salts (anhydrous) in water:

	Free base.	Hydrochloride.	Hydrobromide.
Morphine	$[\alpha]_D^{23} = -130{\cdot}9°$	$[\alpha]_D^{26} = -111{\cdot}5°$	$[\alpha]_D^{20} = -100{\cdot}4$
Chloromorphide	$[\alpha]_D^{27} = -375{\cdot}2$	$[\alpha]_D^{21} = -313{\cdot}7$	$[\alpha]_D^{19} = -268{\cdot}6$
Bromomorphide	$[\alpha]_D^{25} = +65{\cdot}6$	$[\alpha]_D^{27} = +41{\cdot}1$	$[\alpha]_D^{26} = +39{\cdot}5$

are all devoid of narcotic action. The significance of these facts and the relationship between morphine and isomorphine were also discussed.

*90. "On the oxime of mesoxamide and some allied compounds." By Martha Annie Whiteley, B.Sc.

The compound formed by the action of nitrosyl chloride on malonamide (Tilden and Forster, *Trans.*, 1895, 67, 490) appears to be the isonitroso-derivative, $NH_2OC{\cdot}C(NOH){\cdot}CONH_2$. It dissolves readily in water, has an acid reaction, and melts with decomposition at 187°. It forms alkaline salts which are bright yellow in colour and are easily soluble in water. Its most characteristic reaction is the production of an intense purple coloration when neutralised with an alkali and a solution of ferrous sulphate added. This is due to the formation of a double potassium ferrous salt, $KFe(C_3H_4N_3O_3)_3$, which crystallises from concentrated solutions in minute prisms having the lustre of bronze. The acetyl derivative of the oxime resembles the original substance in appearance, and melts with decomposition at 190°. The ethyl ether is crystalline, and melts at 150—151°.

The oxime can be prepared by the action of nitrous acid on the aqueous solution of malonamide, and by the action of hydroxylamine on dibromomalonamide.

By the action of nitrous acid on the oxime, a crystalline, sparingly soluble compound is obtained, which melts with decomposition at about 215°. It contains the proportion of nitrogen corresponding to a pseudonitrol of the formula $CONH_2{\cdot}C\begin{matrix}NO\\NO_2\end{matrix}{\cdot}CONH_2$. It does not respond to Liebermann's test, nor does it react as an oxime. By the continued action of nitrous acid, oxalic acid was the only solid product obtained.

The oxime is reduced by hydriodic acid to aminomalonamide, $CONH_2{\cdot}CHNH_2{\cdot}CONH_2$, the hydriodide of which crystallises in prisms.

The oxime of pyruvamide, $CH_3{\cdot}C(NOH){\cdot}CONH_2$, prepared by the action of ammonia on the oxime of ethyl pyruvate, melts at 176—177° and closely resembles the oxime of mesoxamide, but the alkaline solutions exhibit no decided yellow colour, whilst the colour produced by the addition of ferrous sulphate to the alkaline solution is reddish-brown. In attempting to prepare the oxime of pyruvamide by the joint action of ammonia and hydroxylamine on ethyl pyruvate, the chief product obtained was the oximidohydroxamic acid, $CH_3{\cdot}C{:}NOH{\cdot}C\begin{matrix}NOH\\OH\end{matrix}$, which is readily soluble, melts with decomposition at 143°, and is distinguished, not only by the cherry-red colour which is produced by the addition of ferric chloride, but by the production of an intense reddish-

brown liquid and subsequent precipitate on the addition of ferrous sulphate to the alkaline solution.

Succinamide submitted to the action of nitrosyl chloride or of nitrous acid is attacked but slowly, yielding succinic acid, but no oxime or other derivative.

Attempts to prepare Piutti's β-oxime of the half acid ethylsuccinic ester were not successful; this was apparently due to the spontaneous conversion of the β-compound into Ebert's α-isomeride. Cramer (*Ber.*, 1891, **24**, 1204) represents the β-compound as the stable, and the α- as the labile isomeride.

***91. "On dimethyldiacetylacetone, tetramethylpyrone, and orcinol derivatives from diacetylacetone." By J. N. Collie, F.R.S., and B. D. Steele, M.Sc.**

That dimethylpyrone is capable of acting as a basic substance, forming salts with acids has already been clearly shown (Collie, *Trans.*, 1899, **75**, 710). This work has been continued and the basic properties of tetramethylpyrone have been investigated.

The sodium salt of dimethylpyrone reacts with methyl iodide, giving *dimethyldiacetylacetone*, m. p. 87°, $C_7H_8O_3Na_2 + 2CH_3I = C_7H_8O_3(CH_3)_2 + 2NaI$. When warmed with hydrochloric acid this compound loses water and is converted into *tetramethylpyrone*, $C_7H_8O_3(CH_3)_2 = C_7H_6O_2(CH_3)_2 + H_2O$. Tetramethylpyrone melts at 92°. It crystallises from water as a monohydrate, m. p. 63—64°. It forms a hydrochloride and a platinichloride, but appears to be less basic than dimethylpyrone. From the residues after separation of the dimethyldiacetylacetone, two other substances have been isolated, (1) trimethylpyrone, $C_8H_{10}O_2$, m. p. 78°, which forms a platinichloride; and (2) a derivative of orcinol, $C_9H_{12}O_2$, m. p. 150°, possibly trimethyl-1 : 2 : 4-dihydroxy-3 : 5-benzene.

This orcinol derivative resembles mesorcinol in a very remarkable manner, but it is difficult to see how mesorcinol, which is 1 : 3 : 5-trimethyl-2 : 4-dihydroxybenzene, could be produced from dimethyldiacetylacetone.

A second orcinol derivative, $C_9H_{12}O_2$, was obtained by treating the crude product of the action of methyl iodide on disodiumdiacetylacetone with hydrochloric acid. It melts at 105° and in all its reactions resembles the compound melting at 150°.

Dimethylpyrone unites with sodium ethoxide to form a compound, $C_7H_8O_2NaOEt$, which on treatment with acids yields *ethyldiacetylacetone*, $C_7H_9O_3Et$. This latter substance is very unstable, and easily decomposes into alcohol and dimethylpyrone when heated with acids.

***92. "Dehydracetic acid." By J. N. Collie, F.R.S.**

Since the publication of a paper on dehydracetic acid (Collie and Le Sueur, *Trans.*, 1894, **65**, 254), several reactions and the properties of various compounds of the acid have been investigated, all of which agree with the formula put forward by the author some years ago, namely, that dehydracetic acid is the lactone of tetracetic acid. The production of dehydracetic acid from triacetic lactone has been accomplished, as indicated by the following equation,

$$C_6H_6O_3 + (CH_3CO)_2O = C_8H_8O_4 + CH_3CO_2H.$$

Although neither acetyl chloride nor acetic anhydride react with triacetic lactone alone, if the lactone be boiled with acetic anhydride and a little sulphuric acid or sodium acetate, dehydracetic acid is formed. The action of ammonia on the isomeric acid $C_8H_8O_4$ (obtained by Feist from the dichloride of dehydracetic acid) has been investigated, and an acid, $C_6H_9NO_3$, has been obtained identical with that previously isolated from the products of the action of heat on ethyl β-amidocrotonate.

The production of dehydracetic acid from several of its dried salts has been studied. The dried sodium and silver salts treated with hydrogen chloride, and the dried lead salt with hydrogen sulphide, give dehydracetic acid.

The conductivity of a very pure sample of dehydracetic acid has been determined by Prof. J. Walker, who finds it to be 0·0001.

***93. "The decomposition of hydroxyamidosulphates by copper sulphate." By E. Divers and T. Haga.**

When a hydroxyamidosulphate is heated in solution with copper sulphate it is entirely decomposed. This takes place in such a manner as to throw much light on the nature of the obscure decompositions of these salts, as well as of the hydroximidosulphates and hydroxylamine salts when impure. No change is observed in the copper sulphate during the change it brings about, but of its alternate reduction and oxidation evidence is given, if, instead of the sulphate, cupric chloride be employed, as this is reduced to cuprous chloride.

The principal change caused by the copper sulphate may be represented by the equation $2Cu(H_2NSO_4)_2 = Cu(H_2NSO_3)_2 + Cu(H_2NSO_5)_2$, the latter salt being represented by the actual products $Cu(H_2NSO_5)_2 = N_2O + H_2O + H_2SO_4 + CuSO_4$. Another change always takes place at the same time, being less marked when the temperature is low, and more so when the temperature is high. For example, a hydroximidosulphate resists the action of the copper sulphate until the temperature of

the solution is over 100°, when it hydrolyses to hydroxyamidosulphate, 28 per cent. of which decomposes so that all its sulphur becomes dioxide, its hydrogen water, and its nitrogen nitrous oxide. If one-third of the hydroxyamidosulphate decomposed thus, the reaction would be expressed by the equation, $3Cu(H_2NSO_4)_2 = 2N_2O + 4H_2O + 2SO_2 + 2CuSO_4 + Cu(H_2NSO_3)_2$. Hydroxyamidosulphate decomposing under the influence of copper sulphate may give as little as $3\frac{1}{2}$ per cent. of its sulphur as dioxide. In all cases, the quantity of sulphur appearing as sulphate approximately equals that as amidosulphate. The production of any free nitrogen is still doubtful; it could only be formed when the sulphur as sulphate exceeded in amount that existing as amidosulphate.

***94. "The degradation of glycollic aldehyde." By H. J. H. Fenton.**

As glycollic aldehyde is now obtainable in a pure state (*Trans.*, 1895, 67, 774), experiments are being carried on with a view of studying its relationships and properties. The author showed that by means of Wohl's reaction formaldehyde may readily be obtained from glycollic aldehyde. Glycollic aldoxime is obtained as a syrup from the interaction of the aldehyde and hydroxylamine in alcoholic solution, but it has not been obtained quite pure. When this syrup is mixed with acetic anhydride and sodium acetate, a violent reaction takes place, and the acetyl derivative of glycollic nitrile (b. p. 177°) is formed. This is identical with that obtained by Henry (*Compt. rend.*, 1890, 110, 759—760) from formaldehyde and hydrogen cyanide. When this acetyl derivative is acted upon by the calculated quantity of ammoniacal solution of silver oxide, silver cyanide separates in a crystalline state, and a product is obtained which, with dilute sulphuric acid, yields abundance of formaldehyde.

95. "Notes on the chemistry of chlorophyll." By Leon Marchlewski, Ph.D., and C. A. Schunck.

The authors first discussed the absorption spectrum of unaltered chlorophyll, and conclude (1) that this spectrum is characterised by three bands between the lines B and F and three between F and K_β; (2) that the bands exhibited by crude leaf extracts are caused by one chemical compound, chlorophyll, and not by several substances; (3) that no solution which does not exhibit this spectrum can be said to contain chlorophyll, no matter how it may have been prepared. Unaltered chlorophyll, by the action of hydrochloric acid, ought to give both phylloxanthin and phyllocyanin, the latter most certainly. The authors contend that Hartley's "blue chlorophyll" is not un-

altered chlorophyll, but a derivative closely allied to alkachlorophyll, since its spectrum is quite different from that of unaltered chlorophyll and gives with acids phyllotannin or its derivatives, but neither phylloxanthin nor phyllocyanin.

As to the several "chlorophylls," the authors corroborated the results of Hartley and Sorby's experiments, which tend to show the existence of a colouring matter besides chlorophyll proper and the members of the xanthophyll group. They show, however, that Hartley's "yellow chlorophyll" is a mixture of this additional colouring matter with members of the xanthophyll group, and that by removing the latter its colour is green; the name "yellow chlorophyll" is therefore unsuitable. Crude leaf extracts therefore contain two green colouring matters, chlorophyll proper and another which is present only in *small* quantity; this exhibits a red fluorescence and is characterised by an absorption band in the red which is more refrangible than that of true chlorophyll. The authors described a method by which chlorophyll could be obtained almost free from this green colouring matter, and from the members of the xanthophyll group.

The action of bromine on phylloporphyrin and hæmatoporphyrin is very similar, and this is considered by the authors as an additional proof of the close relationship of these substances.

96. "A new series of pentamethylene derivatives. I." By W. H. Perkin, jun., Jocelyn F. Thorpe, and C. Walker.

When ethyl *aa'*-dibrom-*ββ*-dimethylglutarate,

$$CO_2Et\cdot CHBr\cdot C(CH_3)_2\cdot CHBr\cdot CO_2Et,$$

is treated with an alcoholic solution of potash, it is converted quantitatively into *ethoxycaronic acid*, $(CH_3)_2C\begin{cases}C(OC_2H_5)CO_2H\\CH\cdot CO_2H\end{cases}$, which separates from benzene in long needles melting at 136°; the *anhydride*, made by distilling the acid, boils at 160—165° (50 mm.), and on boiling with water is reconverted into the acid.

When warmed with concentrated sulphuric acid, or when heated with hydrobromic acid in a sealed tube, the acid is converted into the anhydride of *asym*-dimethylsuccinic acid, $(CH_3)_2C\begin{cases}CO\\CH_2\cdot CO\end{cases}O$, which melts at 39°, and on boiling with water yields *asym*-dimethylsuccinic acid melting at 139°.

When ethyl dibromdimethylglutarate is condensed in alcohol solution with an equimolecular proportion of ethyl sodiomalonate, a 60 per cent. yield of an ester of the probable formula

$$(CH_3)_2C\begin{cases}C(CO_2Et)\cdot CH(CO_2Et)_2\\CH\cdot CO_2Et\end{cases},$$

is produced; it is a thick liquid which boils at 234° (20 mm.), and on hydrolysis with alcoholic potash is converted into the *tribasic* acid, $(CH_3)_2C<\begin{matrix}C(CO_2H)\cdot CH_2\cdot CO_2H\\ CH\cdot CO_2H\end{matrix}$, a colourless substance which separates from water in small needles and melts at 176° with evolution of aqueous vapour. When ethyl dibromdimethylglutarate is condensed with 2 equivalents of ethyl sodiomalonate in the presence of excess of sodium ethoxide, a yellow *sodium* compound of the formula $(CH_3)_2C<\begin{matrix}C(CO_2Et)\cdot C(Na)\cdot CO_2Et\\ C(CO_2Et)\cdot CO\end{matrix}$ is produced to the extent of 60 per cent. of the theoretical amount; it is a remarkably stable substance, giving in alcoholic solution a deep red coloration with ferric chloride, and on hydrolysis in the cold with methyl alcoholic potash is converted into the yellow *potassium* compound, $(CH_3)_2C<\begin{matrix}C(CO_2Et)\cdot CK\cdot CO_2Et\\ C(CO_2K)\cdot CO\end{matrix}$, this when acidified, gives the corresponding *acid ester*,

$$(CH_3)_2C<\begin{matrix}C(CO_2Et)\cdot CH\cdot CO_2Et\\ C(CO_2H)\cdot CO\end{matrix},$$

which crystallises from dilute alcohol in large prisms and melts at 75°.

On distilling this acid ester under diminished pressure, carbon dioxide is eliminated, and the *ester*, $(CH_3)_2C<\begin{matrix}C(CO_2Et)\cdot CH\cdot CO_2Et\\ CH\text{——}CO\end{matrix}$, passes over at 201° (30 mm.) as a thick oil which gives an intense violet colour with ferric chloride, and on hydrolysis with potash is converted into the *acid* $(CH_3)_2C<\begin{matrix}C(CO_2H)\cdot CH\cdot CO_2H\\ CH\text{——}CO\end{matrix}$, a colourless substance crystallising from concentrated hydrochloric acid in large prisms and melting at 179°; it gives a red coloration with ferric chloride.

When the sodium compound mentioned above is treated with an equal weight of potash dissolved in ethyl alcohol, it passes into solution, and on boiling deposits a *potassium* salt, of the probable constitution, $(CH_3)_2C<\begin{matrix}C(CO_2K)\cdot CK\cdot CO_2K\\ C(CO_2K)\cdot CO\end{matrix}$; this, on being acidified, yields a mixture of two isomeric acids, which can be separated by recrystallisation from dilute hydrochloric acid. The more soluble acid is identical with the acid mentioned above melting at 179°, the *less soluble acid* crystallises from dilute hydrochloric acid in needles melting at 154—155°, with evolution of carbon dioxide; it gives an intense violet colour with ferric chloride; the first acid is called the α-, the second the β-modification.

Both modifications, the β- on heating above its melting point, the α- on heating with water in a sealed tube at 200°, are quantitatively converted into the *acid*, $(CH_3)_2C<\begin{matrix}C(CO_2H)\cdot CH_2\\ CH\text{——}CO\end{matrix}$, which crystallises

from water in fern-like needles melting at 180° and subliming when heated, in long, silky needles; the *semicarbazone* melts and decomposes at 225°, and the *hydrazone* at 217°.

On reducing the ketonic acid melting at 180° with sodium amalgam it behaves in a remarkable manner, the ketone group remaining intact and the trimethylene linkage being reduced, forming the *acid*, $(CH_3)_2<\begin{matrix}CH\cdot(CO_2H)\cdot CH_2\\ CH_2\text{———}CO\end{matrix}$, which separates from water in microscopic needles melting at 103°; the *semicarbazone* decomposes at 215°.

When the yellow sodium compound mentioned above is treated in alcoholic solution with methyl iodide it is converted into the *ester* $(CH_3)_2C<\begin{matrix}C(CO_2Et)\cdot C(CH_3)CO_2Et\\ C(CO_2Et)\cdot CO\end{matrix}$, a colourless oil boiling at 219° (20 mm.) and giving no coloration with ferric chloride.

On hydrolysis with methyl alcoholic potash, this ester is converted into a potassium salt which when acidified gives the *acid* $(CH_3)_2C<\begin{matrix}C(CO_2H)\cdot C(CH_3)\cdot CO_2H\\ CH\text{———}CO\end{matrix}$, a colourless substance crystallising from benzene in lustrous plates melting at 146°, this, when heated in aqueous solution at 200°, gives the *acid*, $(CH_3)_2C<\begin{matrix}C(CO_2H)\cdot CH(CH_3)\\ CH\text{———}CO\end{matrix}$, which separates from water in glistening plates and melts at 134°; the *semicarbazone* decomposes at 230°.

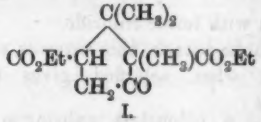
If the potassium salt just mentioned be not separated, but the heating continued, it passes into solution with the formation of *an acid* characterised by being practically insoluble in dry ether, and which differs from the acid melting at 146° in containing 1 mol. of water of constitution. It separates slowly from water in large prisms melting at 237°, and when distilled under ordinary pressure passes over at about 270° as an oil which solidifies on cooling. This on boiling with water is converted into an *isomeric acid* which separates from water in needles melting at 180—181°, with formation of the anhydride.

The reactions of these compounds seem to indicate that they are stereoisomeric furfurane derivatives having the formula $(CH_3)_2C<\begin{matrix}C(CO_2H)\cdot C(CH_3)CO_2H\\ \vert\quad\quad >O\\ CH\text{———}CH(OH)\end{matrix}$.

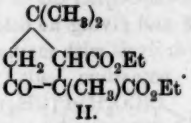
The investigation of these compounds, which are closely allied to several derivatives of the camphor and terpene series, is in progress, and experiments are being carried out in order to study the behaviour of other glutaric acids under the conditions indicated above.

97. "Experiments on the synthesis of camphoric acid. III. The action of sodium and methyl iodide on ethyl dimethylbutanetricarboxylate." By W. H. Perkin, jun., and Jocelyn Field Thorpe.

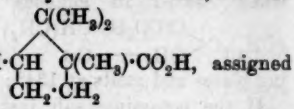
When ethyl dimethylbutanetricarboxylate (*Trans.*, 1899, **75**, 900), dissolved in toluene, is treated with sodium and then with methyl iodide, a considerable yield of an ester is obtained which boils at 168—170° (18 mm.), and on analysis gives numbers agreeing with the formula $C_{14}H_{22}O_5$. The method of formation of this substance clearly indicates that it must have one of the two following constitutional formulæ:



I.



II.

If the ester has the constitution represented by formula I, it must be closely allied to, and will probably be easily converted into, an acid having the constitutional formula  assigned by Bredt to camphoric acid.

On reduction by means of sodium amalgam, this ester is converted quantitatively into a syrupy hydroxy-acid, which on long standing shows signs of crystallising. The analysis of this acid and its silver salt shows that it has the formula $C_{10}H_{16}O_5$; it is therefore isomeric with camphanic acid. The authors are continuing the investigation of these substances.

98. "The oxyphenoxy- and phenylenoxy-acetic acids." By W. Carter and W. Trevor Lawrence.

The phenylenoxyacetic acids, $C_6H_4(OCH_2CO_2H)_2$, are obtained according to either of the following equations:

1. $C_6H_4(ONa)_2 + 2CH_2BrCO_2Et = C_6H_4(OCH_2CO_2Et)_2 + 2NaBr.$
2. $C_6H_4(ONa)_2 + 2CH_2ClCO_2Na = C_6H_4(OCH_2CO_2Na)_2 + 2NaCl.$

The condensation according to the first equation is not complete in the cases of resorcinol and hydroquinol, and a certain amount of acid ester, $C_6H_4(OH)(OCH_2CO_2Et)$, corresponding to the oxyphenoxyacetic acids is formed, and may be separated from the neutral ester by potash solution.

On pouring the esters into alcoholic potash the potassium salts of the acids are precipitated as microcrystalline powders, which when acidified yield the free acids.

The amides are obtained from the esters by shaking with aqueous ammonia, the aniline salts result on boiling the acids with a benzene solution of aniline, and the anilides are obtained by heating the acids to 190° with aniline.

Pyrocatechol derivatives.

Ethyl pyrocatecholdiacetate, $C_6H_4(OCH_2CO_2Et)_2$, boils at 230—232° (30 mm.). *Pyrocatecholdiacetic acid*, $C_6H_4(OCH_2CO_2H)_2$, needles from water, m. p. 178°. *Aniline salt*, m. p. 250°. *Barium salt*, $2(C_{10}H_8O_6Ba),H_2O$. *Pyrocatecholdiacetanilide*, $C_6H_4(OCH_2CONHPh)_2$, m.p. 196°. *Pyrocatecholdiacetamide*, $C_6H_4(OCH_2CONH_2)_2$, m. p. 203°. *Ethyl pyrocatecholmonoacetate*, $C_6H_4(OH)(OCH_2CO_2Et)$, b. p. 155° (30 mm.). *Pyrocatecholmonoacetic acid*, $C_6H_4(OH)(OCH_2CO_2H)$, prisms from water, m. p. 152°. *Anhydropyrocatecholmonoacetic acid*, $C_6H_4<\begin{matrix}O\cdot CH_2\\ O\cdot CO\end{matrix}$, prisms from ligroin, m. p. 57°. *Pyrocatecholmonoacetanilide*, $C_6H_4(OH)(OCH_2CONHPh)$, m. p. 161°. [Compare Moureu, *Bull.*, 1899, [iii], **21**, 107].

Resorcinol derivatives.

Ethyl resorcindiacetate, $C_6H_4(OCH_2CO_2Et)_2$, m. p. 42° (B. 40°), b. p. 228° (32 mm.). *Resorcindiacetic acid*, $C_6H_4(OCH_2CO_2H)_2$, m. p. 195°. The silver, copper, and iron salts are amorphous, the calcium and barium salts crystalline. *Aniline salt*, m. p. 137°. *Resorcindiacetanilide*, $C_6H_4(OCH_2CONHPh)_2$, m. p. 169° (B. ca. 182°). *Imidoester*, $[C_6H_4(OCH_2CO_2Et)OCH_2CO]_2NH$, m. p. 43°. *Resorcindiacetamide*, $C_6H_4(OCH_2CONH_2)_2$, m. p. 167°. *2 : 4 : 6-Trinitroresorcindiacetic acid*, $C_6H(NO_2)_3(OCH_2CO_2H)_2$, is formed by boiling resorcindiacetic acid with nitric acid, m. p. 174°, converted by potash at 140° into styphnic acid. *Resorcinmonoacetic acid*, $3(C_8H_8O_4),H_2O$, m. p. 158°, anhydrous needles from toluene, m. p. 160° (B. 158°). *Resorcinmonoacetanilide*, m. p. 125°.

Hydroquinol derivatives.

Ethyl hydroquinoldiacetate, $C_6H_4(OCH_2CO_2Et)_2$, needles from ligroin, m. p. 72°. *Hydroquinoldiacetic acid*, $C_6H_4(OCH_2CO_2H)_2$, prisms insoluble in all solvents tried except acetic acid, m. p. 251° (B. ca. 246°). *Hydroquinoldiacetanilide*, $C_6H_4(OCH_2CONHPh)_2$, m. p. 210°. The ammonium salt crystallises in needles from water, the silver and copper salts are amorphous, and the calcium and barium salts crystalline.

Hydroquinolmonoacetic acid, $3(C_8H_8O_4),H_2O$, prisms from water, anhydrous needles from toluene, m. p. 152°. *Aniline salt*, m. p. 119°. *Hydroquinolmonoacetanilide*, $C_6H_4(OH)(OCH_2CONHPh)$, m. p. 101°.

The melting points in brackets, and indicated by B, refer to a

private communication from Prof. C. A. Bischoff, who is engaged in the investigation of many of these substances, in pursuance of his "Studies on Condensations," and to whom we therefore relinquish their further study.

99. "The condensation of ethyl α-bromoisobutyrate with ethyl malonates and ethyl cyanacetates: α-methyl α'-isobutylglutaric acid." By W. Trevor Lawrence, B.A., Ph.D.

The author showed that the following general reactions hold good:

I. $CNaRX(CO_2Et) + CBr(CH_3)_2CO_2Et = CRX(CO_2Et)\cdot C(CH_3)_2(CO_2Et) + NaBr$, when the sodium compound is in suspension,

II. $CNaRX(CO_2Et) + CBr(CH_3)_2(CO_2Et) = CRX(CO_2Et)\cdot CH_2\cdot CH(CH_3)(CO_2Et) + NaBr$, when the sodium compound is in solution,

where R = H or an alkyl group; X = (CN) or (CO_2Et).

The behaviour of ethyl bromoisobutyrate is probably influenced by the degree of ionisation of the sodium compound.

The author suggests that the hydrobromic acid liberated from the bromoisobutyric ester combines with (the enolic form of) ethyl sodiomalonate or -cyanacetate to form a hypothetical addition compound, for example, $CN\cdot CHR\cdot C(ONa)(Br)(OC_2H_5)$, which condenses with the unsaturated ester with separation of sodium bromide.

The following substances were isolated and investigated in the course of this research:—

I. In the condensation of ethyl sodioisobutylmalonate with ethyl α-bromoisobutyrate, or ethyl α-methacrylate in alcoholic solution.

Ethyl α-methyl-α'-isobutylpropanetricarboxylate, $CH(CH_3)CO_2Et\cdot CH_2\cdot C(C_4H_9)(CO_2Et)_2$, b. p. 185° (18 mm.), converted by hydrolysis with alcoholic potash into the potassium salt of *α-methyl-α'-isobutylpropanetricarboxylic acid*. This acid melts at 167—168° (with evolution of carbon dioxide and formation of cis- and trans-*methylisobutylglutaric acids*).

The *cis*- and *trans*-methylisobutylglutaric acids, $CH(CH_3)(CO_2H)\cdot CH_2\cdot CH(C_4H_9)CO_2H$, are best separated by crystallisation from boiling ligroin (b. p. 110—120°).

cis-*Acid*, m. p., 121°. *Anhydride*, a liquid, b. p. 196° (50 mm.). *Anilic acid*, $C_{16}H_{23}O_3N$, m. p. 164°.

trans-*Acid*, m. p. 86—87°. *Anhydride*, a liquid, b. p. 178° (22 mm.). *Anilic acid*, m. p. 196°.

The *trans*-acid may be converted into the *cis*-modification by heating

with hydrochloric acid in a sealed tube, or into the *cis*-anhydride by distillation or by heating with acetic anhydride to 220°.

II. In the condensation of ethyl sodioisobutylcyanacetate, b. p. 165° (50 mm.), with ethyl bromoisobutyrate or ethyl *α*-methacrylate in alcoholic solution: in the condensation of ethyl sodiocyanacetate with ethyl methacrylate and subsequent addition of isobutyl bromide.

Ethyl α-methyl-α'-isobutyl-α'-cyanoglutarate,

$$CH(CH_3)CO_2Et\cdot CH_2\cdot C(C_4H_9)(CN)(CO_2Et),$$

b. p. 196° (25 mm.), on hydrolysis with alcoholic potash, is converted into the potassium salt of a substance, $C_{11}H_{17}O_4N$, which melts at 164°, with evolution of carbon dioxide. This substance is possibly a mixture of methylisobutylcyanoglutaric acid with the monocarboxylic acid of methylisobutylglutarimide, as on distillation (295°, 760 mm.) the imide (m. p. 78°) of the *cis*-acid (insoluble in sodium carbonate) and the nitrile of the *trans*-acid are obtained.

It is converted by hydrochloric acid into a mixture of *trans*-glutaric acid and *cis*-glutarimide.

The complete hydrolysis of the nitrile or imide is effected by 50 per cent. sulphuric acid.

III. In the condensation of ethyl bromoisobutyrate with ethyl sodioisobutyl-malonate or -cyanacetate in benzene solution: in the condensation of ethyl bromoisobutyrate with ethyl sodiocyanacetate in alcoholic solution with subsequent addition of isobutyl bromide.

Ethyl aα-dimethyl-α'-isobutyl-α'-cyansuccinate, b. p. 180° (20 mm.), $CO_2Et\cdot C(CH_3)_2\cdot CH(C_4H_9)(CN)(CO_2Et)$, when hydrolysed with alcoholic potash and then acidified, gives a pasty mass of cyano-acid—on complete hydrolysis with 50 per cent. sulphuric acid it gives *aα-dimethyl-α'-isobutylsuccinic acid*, $CO_2H\cdot C(CH_3)_2\cdot CH(C_4H_9)CO_2H$, prisms from water, m. p. 141°.

Experiments on the oxidation of methylisobutylglutaric acid (the study of which was the original object of this research) with potassium permanganate either at 60° or in the cold, showed that the greater part of the acid could be recovered unchanged, the oxidation products consisting of oxalic acid, isobutylmalonic acid, a fatty acid (isobutylacetic acid ?), two liquid acids, of which one appeared to be a hydroxy-acid, $C_{10}H_{18}O_5$, and the other an unsaturated acid, $C_{10}H_{16}O_4$, and a crystalline acid, m. p. 80°, of the same composition.

These acids were obtained in very small quantities and their complete separation was both difficult and probably unsuccessful.

100. "Methylisoamylsuccinic acid. II." By W. Trevor Lawrence, B.A., Ph.D.

The anil of *trans*-α-methyl-α′-isoamylsuccinic acid melts at 118°, and that of the *cis*-acid at 116°.

The partial conversion of the *cis*- into the *trans*-modification may be brought about by heating with hydrochloric acid, and the reverse change by heating the *trans*-acid with acetic anhydride at 210°.

The *cis*-anhydride is converted by phosphorus pentabromide, bromine, and alcohol into ethyl α-bromomethylisoamylsuccinate (b. p. 155°, 20 mm.), $C_{14}H_{25}O_4Br$, which, when poured into hot alcoholic potash forms the potassium salt of isoamylcitraconic acid,

$$CO_2H\cdot C(CH_3):C(C_5H_{11})\cdot CO_2H.$$

Oxidation of methylisoamylsuccinic acid by means of potassium permanganate gave results similar to those obtained by the oxidation of the isomeric methylisobutylglutaric acid (compare preceding abstract); only a small portion of the acid was oxidised by the permanganate, giving oxalic acid, a liquid acid having the formula $C_{10}H_{16}O_4$, and a lactonic acid having the same formula and melting at 103°.

Correction.—Isoamylsuccinic acid melts at 83—84°, not 76° as previously stated (*Proc.*, 1899, **15**, 163).

101. "The estimation of furfural." By William Cormack.

The process proposed by the author is based on the oxidation of furfural to pyromucic acid by means of an ammoniacal solution of silver oxide, according to the equation $C_5H_4O_2 + Ag_2O = C_5H_4O_3 + 2Ag$. The action takes place quantitatively when the solutions are warmed. A known volume of a decinormal silver oxide solution, somewhat in excess of that required for the oxidation of the furfural, is added to the furfural solution, the reduced silver is filtered off through asbestos, and the silver remaining in the filtrate estimated by means of decinormal ammonium thiocyanate.

The method is applicable to furfural solutions such as those derived from fibres by distillation with hydrochloric acid, the furfural being distilled over with steam from the solution after neutralisation with alkaline carbonate, and subsequent slight acidification with oxalic acid.

102. "The constitution of hydrogen cyanide." By John Wade.

When potassium cyanide is heated with alkyl potassium sulphates at a lower temperature than in the preparation of nitriles, the isomeric isocyanide is often the principal product. The author also

has found that practically all the isocyanides can be converted into nitriles by the action of heat. The formation of nitriles in the above interaction is thus accounted for, and one of the arguments in favour of the nitrilic constitution of hydrogen cyanide disappears.

Isocyanides form crystalline products with aldehydes, probably homologous with the aldehyde cyanhydrins, for which the formula $R\cdot\overset{|}{C}H\cdot\underset{|}{C}:NH$ (O, O) is suggested, as the ordinary formula does not account for their anomalous behaviour with alkalis. Compounds have in this way been obtained from acetaldehyde and benzaldehyde in conjunction with methyl-, ethyl- and phenyl-isocyanides.

Isocyanides also form crystalline products with alkyl iodides in presence of alcohol. This interaction accounts for the non-appearance of isocyanides, and probably for the formation of nitriles, when potassium cyanide is heated with alkyl iodides in presence of alcohol. Compounds of this class have been obtained from methyl-, ethyl-, propyl-, isopropyl-, butyl-, isoamyl-, and phenyl-isocyanides in conjunction with methyl, ethyl, propyl, isopropyl, isobutyl, and isoamyl iodides.

n-*Propyl isocyanide*, and n-*butyl isocyanide* do not appear to have been prepared before. They are formed by interaction of the alkyl iodides with silver cyanide, and boil respectively at 97—99° and 118—120° (uncorr.).

103. "Inhibiting effect of etherification on substitution in phenols." By Henry E. Armstrong and Edward W. Lewis.

The inhibiting effect on substitution produced by introducing methyl, ethyl or benzyl in place of the hydroxylic hydrogen in phenolparasulphonic acid has already been referred to (Armstrong, *Proc.*, 1899, 15, 177). At the last meeting of the British Association, it was pointed out that "benzoyl appears to exercise a very remarkable inhibitive effect, as preliminary experiments show that benzoylated phenolparasulphonic acid remains unattacked by bromine under conditions which involve the conversion of the unbenzoylated acid into tribromophenol." This observation has since been confirmed, and the experiments have been extended in order to determine the effect of radicles generally. Besides benzoyl, phenylsulphonyl, $Ph\cdot SO_2\cdot$, benzylsulphonyl, $Ph\cdot CH_2\cdot SO_2\cdot$, and the radicle of Reychler's camphorsulphonic acid, $C_{10}H_{15}O\cdot SO_2\cdot$, afford complete protection against bromine. Picryl, $C_6H_2(NO_2)_3\cdot$, also appears to behave like benzoyl, but owing to the instability of picrylphenolparasulphonate in aqueous solution it is difficult to determine the exact nature of the change effected by bromine. Acetyl, on the other hand, exercises an effect similar to that produced by methyl and ethyl; and the complex radicle phenacyl,

$Ph{\cdot}CO{\cdot}CH_2{\cdot}$, derived from acetophenone, acts much in the same way as acetyl. Difficulty has been experienced in determining the influence of the isomeric radicle phenacetyl, $Ph{\cdot}CH_2{\cdot}CO{\cdot}$, owing to the instability of the ether produced by it; apparently, it also resembles acetyl.

In order to ascertain whether a determining influence is exercised by hydrogen in association with the carbon atom which becomes attached to the phenolic oxygen, tertiary butyl was introduced into phenolparasulphonate. The effect produced by this radicle seems to be altogether different from that of either methyl or ethyl, because on treating the sulphonate with one molecular proportion of bromine, only monobromosulphonate is obtained, the sulphonic radicle remaining intact, but it is displaced by a second molecular proportion of bromine; the methyl and ethyl derivatives are, to a large extent, directly converted into the parabromophenol ethers. In view of this observation it will be necessary to examine other alkyl derivatives.

104. "Bromination of oxyazo-compounds." By Henry E. Armstrong and Percy C. C. Isherwood.

The observations recently made by Hewitt and Aston and by Auwers unquestionably prove that the compound formed by the interaction of phenol and a diazobenzene salt, behaves, in the main, as benzeneazophenol, and there is no doubt that the isodynamic hydrazone comes prominently into evidence only in the presence of acids; it is clear, however, that the equilibrium is easily disturbed in either direction, and that in such a case the constitution *can only* be finally inferred from physical rather than chemical properties.

The authors must confess to having been too much influenced by the extraordinary difference in the behaviour of this compound towards excess of bromine as compared with that of its ethylated derivative, but apparently it is not necessary to infer from this that the two are structurally different, as the principle developed by one of them in discussing the laws which govern substitution in benzenoid compounds suffice to afford an explanation of the dissimilarity.

The conversion of benzeneazophenol into benzeneazodibromophenol and its resolution by excess of bromine into diazobenzene and tribromophenol are comparable with the conversion of phenolparasulphonic acid, first into the dibromosulphonate, and then into tribromophenol and sulphuric acid.

Ethylation exercises an inhibiting influence such as is referred to in the previous abstract, benzeneazophenetol being converted by bromine in presence of sodium acetate only into benzeneazomonobromophenetol. This compound is also formed when a solution of the phenetol in

glacial acetic acid is brominated, but at the same time a "hydrobromide perbromide" is formed which is readily deprived of its bromine by reducing agents. In a previous note (*Proc.*, 1899, **15**, 243), the mistake was made of inferring from observations made with this latter compound that benzeneazo-orthobromophenetol is an easily reducible substance.

As the separation of the azo-group from Hewitt and Aston's benzeneazodiorthobromophenol by bromine is effected even in presence of sodium acetate, it cannot be argued that the scission is consequent on the formation of the hydrazone, and the stability of benzeneazophenetol must therefore be ascribed to the change produced by displacing the hydroxylic hydrogen. The extreme readiness with which the compound assumes the hydrazone form is manifest from the fact that if the sodium acetate be omitted and two molecular proportions of bromine are used, the substance being merely dissolved in acetic acid, benzeneazodiorthobromophenol is mainly resolved into bromodiazobenzene and tribromophenol. Benzoylated benzeneazophenol, like benzoylated phenolparasulphonic acid, is unaffected by bromine.

Clearly, it will be desirable to study further oxy- as well as amidoazo-compounds from the points of view indicated in the preceding abstract.

105. "Meta-sulphonation of aniline." By Henry E. Armstrong and W. Berry.

It has been pointed out by one of the authors that, "in order to produce meta-derivatives from amines, it is necessary to paralyse, as far as possible, the ordinary ortho-para-orientating influence of the amino-group and to give opportunity for the attack to take place in the nucleus" (*Proc.*, 1899, **15**, 177; compare *B. A. Report*, 1899, 685, § 11).

In the case of aniline, sulphuric acid alone appears to be capable of exercising the necessary protective influence, because if the sulphate be dissolved in a large excess of chlorosulphonic acid, the mixture may be heated to 30—40° without any appreciable amount of hydrogen chloride being evolved. Under these conditions, the chlorosulphonic acid is not a sufficiently powerful sulphonating agent to produce even the sulphamate. Consequently, if aniline sulphate be added to a sufficiently strong fuming sulphuric acid, it is in part converted into the meta-sulphonic acid, the nucleus apparently being directly attacked. It is therefore possible to convert aniline into either para- or ortho- or meta-sulphonic acid at will.

106. "Phenylacetylchloramine and analogous compounds." By Henry E. Armstrong.

The author calls attention to the discrepancies in the descriptions given of the properties of phenylacetylchloramine, and discusses the manner in which it undergoes isomeric change.

107. "Benzylanilinesulphonic acids." By Ida Smedley.

These acids have been prepared in order to compare their behaviour with that of the corresponding methyl and ethyl derivatives studied by Miss Evans (*Proc.*, 1895, 11, 235; 1896, 12, 234).

Anilineparasulphonic acid is readily benzylated by digesting an aqueous solution of its sodium salt with benzyl chloride and alkali, the mono- or di-benzyl derivative being formed according to the proportions used. The meta-acid is dibenzylated with extreme readiness.

In their behaviour with bromine, the dibenzylated closely resemble the dimethylated acids. It may therefore be assumed that benzyl does not promote the displacement of the sulphonic group as it does when introduced into phenolparasulphonic acid in place of the hydroxylic hydrogen, but it undoubtedly has an influence different from that exercised by either methyl or ethyl. Thus it is characteristic of dimethyl- and diethyl-sulphanilic acids that, when acted on by bromine, each is converted into an ortho-brominated acid capable of combining with bromine to form a comparatively stable perbromide. The dibenzyl acid yields a similar monobrominated acid, but this does not form a perbromide; it is, however, very easily deprived of its benzyl by the further action of bromine.

108. "Benzeneorthodisulphonic acid." By Henry E. Armstrong and S. S. Napper.

The authors have prepared benzeneorthodisulphonic acid by applying Leuckart's xanthate method (*J. pr. Chem.*, 1890, 41, 179) to parabromanilineorthosulphonic acid. A series of compounds has thus been obtained corresponding with those prepared by Miss Walter (*Proc.*, 1895, 11, 141) from sulphanilic acid.

Potassium parabromophenylxanthateorthosulphonate is easily soluble in water, from which it crystallises with 10 molecules of water.

When hydrolysed by means of sulphuric acid or alcoholic potash, it yields the corresponding thiophenolsulphonic acid, $C_6H_3Br(SH)\cdot SO_3H$, or its potassium salt, the thiophenetolsulphonate, $C_6H_3Br(SEt)\cdot SO_3K$, being also formed when it is hydrolysed by aqueous potash, and when it is decomposed by heating at about 200°.

Bromobenzene-3 : 4-disulphonic acid is conveniently prepared by directly oxidising the xanthate with potassium permanganate. Its sulphochloride crystallises in monosymmetric prisms melting at 88°. The amide crystallises in brilliant anorthic prisms; the anilide in monosymmetric plates melting at 182°. It is converted into benzeneorthodisulphonic acid by boiling its aqueous solution with soda and zinc dust.

Sodium benzeneorthodisulphonate is very soluble in water, from which it crystallises in long, transparent prisms. The barium salt is sparingly soluble even in hot water, and crystallises in glistening plates.

Unlike 1:2-naphthalene-1:2-orthodisulphonic acid, but like toluene-3:4-disulphonic acid, benzeneorthodisulphonic acid is converted into the corresponding chloride by phosphorus pentachloride. This crystallises in magnificent monosymmetric prisms melting at 143°.

The corresponding amide and anilide also crystallise in monosymmetric prisms, the former melting at 252°, the latter at 241°.

A comparison of the acid with phthalic acid is being made.

109. "An isomeride of furfurine." By J. P. Millington, B.Sc., and H. Hibbert, B.Sc.

By the application of the method of Japp and Moir (*Trans.*, 1900, **77**, 637) for the preparation of isoamarine from amarine the authors have succeeded in preparing an isomeride of furfurine. It crystallises from water in needles melting sharply at 143° (furfurine melts at 116°) and on analysis was found to correspond with the formula $C_{15}H_{12}N_2O_3$. A platinichloride and silver derivative have been obtained of which the formulæ are $(C_{15}H_{12}N_2O_3)_2H_2PtCl_6$ and $C_{15}H_{11}N_2O_3Ag$ respectively.

110. The mono- and di-acetyl and phenacetyl diethyl tartrates. By J. McCrae and T. S. Patterson.

The preparation of monoacetyl, diacetyl, monophenacetyl, and diphenacetyl diethyl tartrates was described. Considerable difficulty was experienced in the purification, and different methods had to be adopted in each case. The specific rotation of these substances has been determined at various temperatures with the following results :—

Monoacetyl diethyl tartrate	$[\alpha]_D^{20}$	$+9{\cdot}30°$
Diacetyl " "	$[\alpha]_D^{100}$	$+6{\cdot}30°$
Monophenacetyl " "	$[\alpha]_D^{20}$	$+30{\cdot}38°$
Diphenacetyl " "	$[\alpha]_D^{20}$	$+17{\cdot}92°$

A comparison is instituted, on the one hand, between the series of

monoacidyl tartrates, where it is shown that the phenacetyl radicle exerts a much greater influence than that exerted by the acetyl radicle, and, on the other hand, between the members of the series of diacidyl tartrates where the acetyl and phenacetyl radicles behave similarly but very differently from the toluyl radicles.

The regularity of the influence exerted by the successive introduction of two acidyl groups is noticed. The first acidyl group increases the rotation of the diethyl tartrate, but the second acidyl group diminishes the rotation of the monoacidyl compound.

NILSON MEMORIAL LECTURE.

The Nilson Memorial Lecture will be delivered by Professor Otto Pettersson, of Stockholm, on the evening of Thursday, July 5th, 1900. The Chair will be taken at 8.30.

LIBRARY.

The Library will be closed for stock-taking during the first fortnight of August. Fellows are requested to return all Library books in their possession before July 28th.

RICHARD CLAY AND SONS, LIMITED, LONDON AND BUNGAY.

Issued 7/11/1900

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 16. No. 227.

July 5th. Extra Meeting. Professor THORPE, C.B., F.R.S., President, in the chair.

Professor OTTO PETTERSSON, of Stockholm, delivered the Nilson Memorial Lecture.

On the motion of Dr. ARMSTRONG, seconded by Professor DEWAR, a vote of thanks was passed to Professor Pettersson for his Lecture.

The following are abstracts of the papers received during the vacation, and published in the *Transactions* :—

111. "Asymmetric optically active sulphur compounds; *d*-methylethylthetine platinichloride." By W. J. Pope and S. J. Peachey.

Although the earlier attempts of the authors to resolve methylethylthetine into optically active components were unsuccessful, they have since succeeded in preparing *d*-methylethylthetine platinichloride. Methylethylthetine bromide was treated with silver *d*-camphorsulphonate. The residue, after evaporation at a low temperature, was dissolved in absolute alcohol and precipitated by the addition of anhydrous ether, and this treatment repeated about 40 times, when a sparingly soluble fraction was obtained, which seems to be *d*-methylethylthetine *d*-camphorsulphonate. It melts at 118—120°, and gives $[\alpha]_D = +18{\cdot}6°$ and $[M]_D = +68{\cdot}0°$.

The *d*-bromocamphorsulphonate was similarly prepared. When either of these salts is dissolved in absolute alcohol, a little strong hydrochloric acid and an alcoholic solution of platinic chloride

added, a yellow, crystalline platinichloride is deposited, having the constitution $2\begin{matrix}C_2H_5\\Cl\end{matrix}\!>\!S\!<\!\begin{matrix}CH_2\cdot CO_2H\\CH_3\end{matrix}, PtCl_4$, and giving $[\alpha]_D = +4{\cdot}5°$ and $[M]_D = +30{\cdot}5°$.

112. "Sulvanite, a new mineral." By G. A. Goyder.

This mineral was found in considerable quantity in some ore from a new mine near the Burra in South Australia. It appears to afford the first recorded instance of a sulphide mineral containing vanadium as one of its principal constituents.

The analyses given show that it consists of cuprous sulphovanadate, $3Cu_2S, V_2S_5$. Its hardness is 3·5, and its specific gravity 4·0.

113. "Estimation of atmospheric carbon dioxide." By James Walker.

A modification of Pettenkofer's bottle method is described which gives results accurate to 0·1 vol. carbon dioxide in 10,000 vols. air, when a bottle of 2·6 litres capacity (Winchester quart) is employed. The usual error due to absorption of carbon dioxide during titration is avoided by filtering the residual baryta solution into a known quantity of hydrochloric acid, and titrating back with standard baryta. The filtration takes place under diminished pressure through asbestos contained in a Soxhlet filter tube, atmospheric air being entirely excluded during the process of filtering and washing. No special apparatus is employed, and an estimation occupies only half an hour.

114. "On some periodides of substituted oxonium derivatives." By J. N. Collie, F.R.S., and B. D. Steele, B.Sc.

During the investigation of the salts of tetramethylpyrone, it was noticed that when the solution of the iodide was allowed to evaporate in the air brownish crystals slowly separated, which were nearly insoluble in water. From their properties they seemed to resemble the periodides of the pyridine bases. It was found that when free iodine in potassium iodide solution was added to a solution of the hydriodide of tetramethylpyrone or of dimethylpyrone, an immediate crystalline precipitate was produced.

These periodides have the following constitution: from dimethylpyrone, $C_7H_8O_2HI,I_2$; from tetramethylpyrone, $C_9H_{12}O_2HI,I_2$. They lose iodine when heated, and are at once converted into di- and tetra-methylpyrone when treated with a solution of soda.

The action of iodine on the barium and sodium salts of dimethyl-

pyrone proceeds in a quite different manner. The chief product is an oxidised iodine compound, $C_7H_7IO_3$, which possesses rather remarkable properties; it is not decomposed when warmed with solutions of soda or sodium ethylate, but gives free iodine at once when warmed with a mineral acid.

115. **"Condensation of phenols with esters of the acetylene series. II. Action of phenols on ethyl phenylpropiolate and ethyl acetylenedicarboxylate." By Siegfried Ruhemann and Fred Beddow.**

The authors describe ethyl-β-*m*-cresoxycinnamate and the products of its transformation as well as the reaction between phenols and ethyl acetylenedicarboxylate. They find that in the latter case aryl ethers of ethyl hydroxyfumarate are formed, and not the ethers of ethyl hydroxymaleate, which were expected; this has been proved by a comparison of the products with the compounds obtained by the action of the sodiophenolates on ethyl chlorofumarate. The aryl ethers of ethyl hydroxyfumarate, on hydrolysis with alcoholic potash, give the corresponding acids, which on heating are partially transformed into the aryl ethers of hydroxymaleic acid; these differ from their stereoisomerides in that lead acetate gives with their aqueous solutions precipitates of their lead salts, but not with the aryl ethers of hydroxyfumaric acid.

116. **"The vapour pressures, specific volumes, and critical constants of di-isopropyl and di-isobutyl. By Sydney Young, D.Sc., F.R.S., and Emily C. Fortey, B.Sc.**

The results here given, taken in conjunction with those of previous researches, show that an iso- or di-iso-paraffin bears very much the same relation to the isomeric normal paraffin as a lower does to a higher homologue. Thus the ratios of the absolute temperatures to the absolute critical temperatures, and of the volumes of saturated vapour to the critical volumes at corresponding pressures, as well as of the actual to the theoretical densities at the critical points, are higher for the normal paraffins, whilst the ratios of the volumes of liquid to the critical volumes at corresponding pressures are lower.

It was found that di-isopropyl shows marked peculiarities; it is exceptionally difficult to prepare by any method involving the combination of two $(CH_3)_2CH\cdot$ groups; the specific gravity at 0° and the critical pressure are higher than those of normal hexane, whereas these constants in all other known cases are lower for the iso- and di-iso-paraffin than for the normal isomerides; the critical density, the critical temperature, and the boiling point are also exceptionally high.

117. "The vapour pressures, specific volumes and critical constants of normal octane." By Sydney Young, D.Sc., F.R.S.

The normal octane was obtained from Kahlbaum, and was easily purified by treatment with sulphuric and nitric acids and subsequent fractional distillation.

A comparison of the data for normal pentane, hexane, heptane and octane shows that the ratios of the absolute temperatures at any series of corresponding pressures to the absolute critical temperatures, and also the ratios of the actual to the theoretical densities at the critical points, increase slightly with rise of molecular weight, whilst the ratios of the volumes of liquid at corresponding pressures to the critical volumes diminish slightly.

The ratios of the volumes of saturated vapour to the critical volume are, on the whole, very slightly lower than for normal heptane, but are higher than for hexane or pentane.

118. "Separation of neobornylamine from bornylamine." By M. O. Forster, and J. Hart-Smith, A.R.C.S.

In the course of attempts to separate neobornylamine from bornylamine, in addition to the *hydrobromide*, *hydriodide*, *nitrate*, *sulphate*, and *benzoate* of bornylamine, the following substances have been obtained.

Camphoroximeacetic acid, $C_{10}H_{16}{:}NO{\cdot}CH_2{\cdot}CO_2H$, which melts at 100—102°, and gives $[\alpha]_D = -5{\cdot}9°$; the *sodium* and *bornylamine* salts are well defined.

Bornyloxamide, $C_{10}H_{17}{\cdot}NH{\cdot}CO{\cdot}CO{\cdot}NH_2$, melting at 162°, which gives $[\alpha]_D = -24{\cdot}1°$.

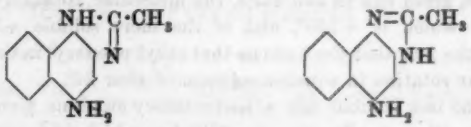
Dibornyloxamide, $C_{10}H_{17}{\cdot}NH{\cdot}CO{\cdot}CO{\cdot}NH{\cdot}C_{10}H_{17}$, which melts somewhat indefinitely at 140°, and gives $[\alpha]_D = -29{\cdot}6°$.

Purified neobornylamine melts at 184°, and has $[\alpha]_D = -43{\cdot}7°$ in absolute alcohol. The *benzylidene* derivative is an oil which boils at 180° under 25 mm. pressure.

119. "Aminoamidines of the naphthalene series." By Raphael Meldola, F.R.S., and Lewis Eynon, A.I.C.

It has been found by the authors that when dinitro-α-acetnaphthalide is reduced by iron and hydrochloric acid (Markfeldt, *Ber.*, 1898, **31**, 1174), the ethenyltriaminonaphthalene produced is isomeric and not identical with that obtained when tin and hydrochloric acid are used (Meldola and Streatfeild, *Trans.*, 1887, **51**, 691). In this paper it is shown that the isomerism is entirely attributable to the reducing

agent, since the same dinitro-α-acetnaphthalide has been used throughout. Descriptions and analyses are given of Markfeldt's base and some of its salts, of the acetyl derivatives of both bases and their salts and of the isomeric phenylazo-derivatives. The pronounced difference in the properties of the latter compounds first indicated the isomerism of the respective anhydro-bases. It is suggested that the isomerism may be explained by the structural differences indicated by the formulæ :



Experiments with the object of determining the constitution of the amino-amidines have been commenced, and the research will be extended in this direction. When the NH_2 group in Markfeldt's base is replaced by hydrogen by the diazo-method an ethyldiamino naphthalene is obtained which is apparently identical with that Prager (*Ber.*, 1885, **18**, 2161).

120. "Note on the elimination of a nitro-group during diazotisation." By Raphael Meldola, F.R.S., and Elkan Wechsler.

When acetorthoanisidide is nitrated with excess of fuming nitric acid in the cold in acetic acid solution, a dinitroacetanisidide is formed. This compound crystallises in light yellow needles melting at 162—163°, and on hydrolysis by alcoholic sodium hydroxide gives a dinitroanisidine, crystallising in bright orange needles having a melting point of 186—188°. This dinitroanisidine, on treatment with sodium nitrite and an acid, forms a diazo-compound which crystallises in ochreous scales or yellow needles, having an exploding point of about 178°. The diazo-compound has the formula $NO_2 \cdot C_6H_3(OCH_3) \cdot N_2 \cdot OH$, so that one nitro-group is eliminated during the process of diazotisation. The corresponding iodonitromethylresorcinol crystallises in flat, yellow needles melting at 115—116°. The nitroazo-β-naphthol derivative, obtained by combining the diazo-compound with β-naphthol in alkaline solution, forms glittering, bronzy-green scales decomposing at about 250°. The constitution of the new dinitroanisidine is being investigated with the object of determining the particular configuration which is favourable to this easy displacement of a nitro-group.

121. "A contribution to the stereochemistry of sulphur; an optically active sulphine base." By S. Smiles, B.Sc.

Methyl ethyl sulphide unites with ω-bromacetophenone to form *methyl-ethyl-phenacylsulphine bromide*, $\begin{matrix}CH_3\\C_2H_5\end{matrix}\!\!>\!S\!<\!\begin{matrix}CH_2COPh\\Br\end{matrix}$; this, when treated in alcoholic solution with silver dextro-α-bromocamphor-sulphonate, gives rise to two salts, the molecular rotation of the less soluble of which is +250°, and of the more soluble +289°. This points to the fact that the basic methyl ethyl phenacyl radicle possesses a molecular rotation in aqueous solution of over 20°.

From the less soluble salt a lævorotatory sulphine picrate was obtained as yellow needles (m. p. 125°) for which $[\alpha]_D = -9{\cdot}3°$ and $[M]_D = -39{\cdot}3°$. The dextrorotatory picrate obtained from the more soluble salt (yellow needles, m. p. 123—124°) gave $[\alpha]_D = +8{\cdot}1°$ and $[M] = +34{\cdot}2$.

It was not found possible, however, to separate two stereoisomers from methyl-ethyl-desyl-sulphine bromide, $\begin{matrix}CH_3\\C_2H_5\end{matrix}\!\!>\!S\!<\!\begin{matrix}CHPh{\cdot}COPh\\Br\end{matrix}$, which was obtained as a colourless mass of deliquescent needles.

122. "Condensation of phenols with esters of the acetylene series. Synthesis of benzo-γ-pyrone." By S. Ruhemann and H. E. Stapleton.

By the condensation of guaiacol and thiophenol with esters of the acetylene series the authors have obtained

$C_6H_5{\cdot}C(OC_6H_4{\cdot}OCH_3){:}CH{\cdot}CO_2Et$ and $C_6H_5{\cdot}C(SC_6H_5){:}CH{\cdot}CO_2Et$;
Ethyl β-*o*-methoxyphenoxycinnamate. Ethyl β-thiophenylcinnamate.

these esters, on hydrolysis with alcoholic potash, give the corresponding acids which lose carbon dioxide and yield respectively

$C_6H_5{\cdot}C(OC_6H_4OCH_3){:}CH_2$ and $C_6H_5{\cdot}C(SC_6H_5){:}CH_2$.
o-Methoxyphenoxystyrene. Thiophenylstyrene.

Ethyl acetylenedicarboxylate condenses with thiophenol to ethyl thiophenylfumarate, which is decomposed by alcoholic potash, forming phenyl disulphide $(C_6H_5S)_2$. Along with the ethyl thiophenylfumarate, ethyl dithiophenylsuccinate is also formed, having probably the formula $CO_2Et{\cdot}C(SC_6H_5)_2{\cdot}CH_2{\cdot}CO_2Et$. The analogous oxygen compound, along with ethyl β-phenoxyfumarate, is obtained by the action of phenol on ethyl acetylenedicarboxylate.

Ethyl β-phenoxycinnamate, by treatment with strong sulphuric acid, is not condensed into flavone, but decomposes into benzoylacetic acid

along with oxalic and acetic acids. Ethyl phenoxyfumarate, however, partially undergoes the desired change, forming benzo-γ-pyronecarboxylic acid, which, on heating, loses carbon dioxide, giving benzo-γ-pyrone, $C_6H_4<^{CO\cdot CH}_{O-CH}$, melting at 59°.

123. "Contributions to the chemistry of hydrotetrazines and triazoles." By Oswald Silberrad, Ph.D.

The action of hydrazine hydrate on diacetanilide gives dimethyldihydrotetrazine, $CH_3C<^{NH\cdot N}_{N\cdot NH}>CCH_3$; its hydrochloride melts at 232°. Benzoyl chloride decomposes it with the formation of *sym*-dibenzoyl-hydrazine and acetic acid.

Nitrous acid converts it into dimethyltriazole nitrate (m. p. 125°), from which the hydrochloride (m. p. 199°) and the free base, $CH_3C<^{NH\cdot N}_{N}>CCH_3$ (m. p. 142°, b. p. 258° at 752 mm.), may be obtained. Its constitution is evident from its synthesis from acetamide and acetylhydrazine,

$$CH_3C<^{NH\cdot NH_2O}_{O\quad H_2N}>CCH_3 = CH_3C<^{NH\cdot N}_{N}>CCH_3 + 2H_2O.$$

Diphenyldihydrotetrazine, $C_6H_5C<^{NH\cdot N}_{N\cdot NH}>CC_6H_5$, may be obtained in almost theoretical quantity by heating benzoylhydrazine with hydrazine hydrate to 230°. It melts at 264°. Pinner gives 258° (*Ber.*, 1894, **27**, 1006).

Heated alone, benzoyl-hydrazine yields only traces of diphenyl-hydrotetrazine, the chief products being diphenyltriazole, $C_6H_5C<^{N\cdot N}_{NH}>C\cdot C_6H_5$, and diphenyl diazoxole, $C_6H_5C<^{N\cdot N}_{O}>CC_6H_5$.

aa-Benzoylphenylhydrazine under similar treatment does not condense, but breaks down with production of benzophenone, benzoic acid and benzoylanilide.

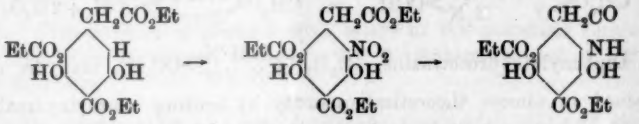
124. "Isomeric dibenzylketone benzalanilines and deoxybenzoin-benzalanilines." By Francis E. Francis, Ph.D., B.Sc.

Three isomeric addition products of the two ketones, dibenzyl ketone and deoxybenzoin, with benzalaniline are described. For the sake of convenience these are termed α-, β-, γ-modifications. The α- is obtained from the pure ketone, the β- by the action of traces of piperidine on the α- or with greater difficulty on the γ-, the γ- by the action of traces

of sodium ethylate on either the α- or β-. By the action of heat, the β- and γ- are transformed into the α-modification. The dibenzyl ketone benzalanilines are more basic than the deoxybenzoin benzalanilines, the former yield normal, whilst the latter give basic hydrochlorides. These salts are different in the case of α- and β- but identical in β- and γ-. They are dissociated by water, giving the corresponding base, but with alcohol the α-hydrochloride appears to give a mixture of α- and γ-base, whereas the β- or γ- gives the α-modification nearly pure.

125. "Condensation of methylic acetonedicarboxylate. Constitution of orcinoltricarboxylic esters." By F. W. Dootson, M.A.

It is shown that a moderate temperature is sufficient to condense methyl acetonedicarboxylate to trimethyl orcinoltricarboxylate, and that a good yield of the latter is obtained. The constitution assigned to ethyl orcinoltricarboxylate by Jerdan is confirmed, and the similarity of the methyl and ethyl esters is shown by nitration and subsequent reduction, when a lactam structure results in both cases, proving that in orcinoltricarboxylic esters the remaining hydrogen atom of the benzene nucleus is in the ortho-position to the side chain, thus :



126. "Contribution to the chemistry of the aromatic meta-diamines." By G. F. Morgan, D.Sc.

In this paper the following compounds are described: 1-*bromo*-2 : 4-*phenylenediamine* melting at 111—112°; its *dibenzoyl* and its *diacetyl* derivatives melting at 178·5° and 198° respectively; *dibenzoyl* 1-*chloro*-2 : 4-*phenylenediamine*, m. p. 178°, and *chlorochrysoidine*, $PhN_2C_6H_2Cl(NH_2)_2$, m. p. 149°; m-*phenylenediacetyldichloramine*, $C_6H_4(NCl{\cdot}Ac)_2$, m. p. 150—151°; *diacetyl*-1 : 5-*dichloro*-2 : 4-*phenylenediamine*, m. p. above 260°; 1 : 5-*dichloro*-2 : 4-*phenylenediamine* melting at 136—137° and its *dibenzoyl* derivative at 187°.

Diacetyl-*m*-toluylenediamine, when chlorinated and then hydrolysed, gives 5-*chloro*-2 : 4-*tolulylenediamine*, m. p. 120—121°; its *diacetyl* derivative melts at 239—240°.

127. "Action of aromatic aldehydes on derivatives of β-naphthylamine." By Gilbert Thomas Morgan, D.Sc.

The *compound*, $C_{48}H_{42}N_2O_2$, produced by the condensation of ethyl β-naphthylamine (2 mols.) with benzaldehyde (3 mols.), crystallises in colourless leaflets and melts at 148°. Its constitution may be represented by one of the following formulæ: $Ph{\cdot}CH(NEt{\cdot}C_{10}H_7)_2$, $2Ph{\cdot}COH$; $C_{10}H_7NEtCHPh{\cdot}O{\cdot}CHPh{\cdot}NEt{\cdot}C_{10}H_7$, $PhCOH$; $PhCH<\begin{matrix}O{\cdot}CHPh{\cdot}NEt{\cdot}C_{10}H_7\\O{\cdot}CHPh{\cdot}NEt{\cdot}C_{10}H_7\end{matrix}$. Its general behaviour is in accordance with the third of these; but freezing point determinations seem to indicate that the substance, dissolved in benzene, corresponds with the second formula.

The following anhydro-bases and their hydrocyanides, derived from 1-chloro-2-naphthylamine and its bromine analogue, are also described in the paper: *benzylidene-1-bromo-2-naphthylamine*, m. p. 93—94°, and its *hydrocyanide*, m. p. 92°; the *cuminylidene* derivative and its *hydrocyanide*, melting at 100—101° and 120° respectively; the p-*hydroxybenzylidene* and o-*hydroxybenzylidene* derivatives, melting respectively at 189—190° and 144°, and the corresponding *hydrocyanides* at 144° and 152°; p-*methoxybenzylidene-1-bromo-2-naphthylamine* and its *hydrocyanide*, melting at 107° and 140—143°; *cinnamylidine-1-bromo-2-naphthylamine*, m. p. 126°, and its *hydrocyanide*, m. p. 142—143°; *benzylidene-1-chloro-2-naphthylamine* and the corresponding *cuminylidene* derivative, melting respectively at 99° and 85°, and their *hydrocyanides* at 77° and 117°; *cinnamylidene-1-chloro-2-naphthylamine*, m. p. 134°, and its *hydrocyanide*, m. p. 155—156°; p-*hydroxybenzylidene-1-chloro-2-naphthylamine* and the corresponding *ortho-isomeride*, melting respectively at 191° and 153°, and their *hydrocyanides* at 152° and 148°; p-*methoxybenzylidene-1-chloro-2-naphthylamine*, m. p. 117°, and its *hydrocyanide*, m. p. 132°.

The following anhydro-bases do not combine with hydrogen cyanide: o-*nitrobenzylidene-1-chloro-2-naphthylamine*, m. p. 142°, and the corresponding *bromo*-compound, melting at 138°; p-*nitrobenzylidene-1-chloro-2-naphthylamine*, m. p. 151°, and its bromine analogue, melting at 154—155°.

128. "Action of hydrogen peroxide on carbohydrates in the presence of ferrous salts. II." By R. S. Morrell, M.A., Ph.D., and J. M. Crofts, M.A., B.Sc.

Rhamnose when oxidised by hydrogen peroxide in the presence of ferrous sulphate yields an osazone which reacts with phenylhydrazine at the ordinary temperature to give rhamnosazone.

Similarly, cane sugar, when the hydrogen peroxide is neutral, is first 'inverted' and then oxidised, since on testing with phenylhydrazine, glucosazone is precipitated.

The action of potassium persulphate on glucose in the presence of ferrous sulphate is slow at ordinary temperatures. On warming to 40°, oxidation proceeds more rapidly with formation of glucosone. The yield of the glucosone (measured by the weight of the glucosazone precipitate) is smaller than when hydrogen peroxide is employed as the oxidising agent.

129. "The specific gravities of the halogens at their boiling points, and of oxygen and nitrogen." By J. Drugman, Ph.D., and W. Ramsay, F.R.S.

The determinations made by the authors of the specific gravities of the halogens at their respective boiling points under atmospheric pressure have given the following results:

Iodine	boiling at	184·5°	has the sp. gr.	3·706
Chlorine	„	−33·6°	„ „	1·507
Fluorine	„	−187°	„ „	1·108

The specific gravity of fluorine was arrived at by using the data of Moissan and Dewar (*Proc.*, 1897, **13**, 180) and calculating the specific gravity at its boiling point, corrections being made for the expansion of the liquid fluorine and the change in the specific gravity of amber. Amber was found to have the specific gravity 1·065 at 15° and 1·10 at −187°. The specific gravities of oxygen and nitrogen were found to be 1·1315 and 0·7914 at their respective boiling points.

130. "On hydroferrocyanic acid." By K. C. Browning, B.A.

The purification and some of the properties of hydroferrocyanic acid are described. This acid begins to evolve hydrocyanic acid at 120°, and its decomposition is complete at 300°, ferrous cyanide being left as a pale yellow powder. Ferrous cyanide decomposes above 430° into iron, carbon and iron carbide. Reasons are given for considering it to be an isocyanide, but when strongly heated it seems to decompose partly as if it were a normal cyanide.

From the decomposition of ethyl ferrocyanide it would seem that all the cyanogen groups present have the isocyanide arrangement.

131. "On the nature of metal-ammonia compounds in aqueous solution. Part I." By H. M. Dawson and J. McCrae.

The nature of various ammoniacal salt solutions has been studied by determining the amount of ammonia extracted by shaking a known

volume of the aqueous solution with a known volume of chloroform. If pure aqueous ammonia be shaken with chloroform at a constant temperature till equilibrium is established, this condition is characterised by the relationship $c_1/c_2 = \text{constant}$ (26·3), where c_1 = concentration of ammonia in water and c_2 that in chloroform.

When this is done with ammoniacal solutions of cupric sulphate, cupric chloride, zinc sulphate, cadmium iodide, and nickel sulphate, the constant is found to give much higher values, and hence the amount in combination with the salt may readily be deduced. Experiments with calcium chloride solution also indicate the formation of a complex metal-ammonia compound, but the amount of ammonia combined per molecule of salt is very much smaller than in the case of the other salts investigated.

Experiments were also made with ammoniacal copper oxide solution which indicate that the base $Cu(NH_3)_2(OH)_2$ is probably formed; the copper sulphate compound has the formula $Cu(NH_3)_4SO_4$.

November 1st, 1900. Professor THORPE, C.B., F.R.S., President, in the Chair.

Messrs. S. S. Napper, G. E. Tomlins, O. Silberrad, C. Watson, C. T. F. Watts, and H. F. F. B. Fermor were formally admitted Fellows of the Society.

The following certificates were read for the first time:—Messrs. George Lowe Bennett, 13 St. Domingo Vale, Egerton, Liverpool; Frederick Nisbet Binks, 2 Hollywell Terrace, Millbourne Avenue, Drumcondra, Dublin; Herbert James Singleton Boyes, 9 Rua Episcopal, São Paulo, Brazil; Theodore Ridley Burnett, 83 Coltart Road, Liverpool; John Henry Cheesewright, 80 Sydney Road, Hornsey, N.; Albert Walker Comber, Rio Marina, I. d'Elba, Italy; Alexander Davidson, jun., 1 Almond Bank Terrace, North Merchiston, Edinburgh; Arthur Louis William Fechtner, 186 Spring bank, Hull; Willie Ludford Freeman, 102 Marlboro' Road, Oxford; William Gasson, Kimberley, South Africa; George William Gibbings, Standard Bank of South Africa, Ltd., Salisbury, Mashonaland; John Gibson, Battle Hill, Hexham, Northumberland; Walter Augustus Handcock, Southbank, 40 Avenue Road, Highgate, London; William Arthur Hargreaves, Port Adelaide, South Australia; George Harker, 35 Boulevarde, Petersham, Sydney, N.S.W. Frank C. R. Hemingway, Albyns, Forest Road, Walthamstow; John Brownlie Henderson, Brisbane, Queensland; Samuel Hewitt, 3 Chester Street, Norwich; William Henry Hewitt, 115 Fentiman Road, London, S.W. Adolf

Jappé, Broad Oak, Oak Avenue, Bradford; Humphrey Owen Jones, Clare College, Cambridge; George Washington Kilner, 14 St. John's Park, Upper Holloway, N.; Morris Charles Lamb, Herold's Institute, Drummond Road, Bermondsey, London, S.E.; George Druce Lander, 1 Balmoral Road, Nottingham; William McCall, Rio Marina, Isola d'Elba, Italy; Thomas Marginson Nightingale, 375 Bridgman Street, Bolton; Alexander Pardy, Pietermaritzburg, Natal, S. Africa; John Paul, Bacteriological Institute, Grahamstown, Cape Colony; Ernest Vivian Pearce, The Beeches, Hayle, Cornwall; Henry Ernest Stapleton, St. John's College, Oxford; Arthur Lambert Thornton, 2 Park Street Bolton; Ferdinand Gerhard Wiechmann, 771 West End Avenue, New York; George Sampson Valentine Wills, Southwood, Croham Road, South Croydon; Walter Bourne Woodbridge, Grey Friars, Chichester; Herbert Edwards Wright, 1 Brewers Street, St. Aldates', Oxford.

Of the following papers, those marked * were read:—

*132. "Action of alkalis on nitro-compounds of the paraffin series. Part II. The reactions and constitutions of methazonic acid and the formation of isoxazoles." By Wyndham R. Dunstan, F.R.S., and Ernest Goulding, B.Sc.

In a previous paper (Dunstan and Dymond, *Trans.*, 1891, **59**, 410) it was shown that trimethylisoxazole results from the action of alkalis on nitroethane, and triethylisoxazole from a similar action on nitropropane. Nitromethane, however, furnished no isoxazole, neither did secondary nitropropane.

Further investigation has shown that the action of alkalis, preferably ammonia, on nitromethane leads to the production of the substance briefly described by Lecco under the name of *methazonic acid*, $C_2H_4N_2O_3$, and regarded by him as an anhydride of nitromethane. The authors have obtained this substance in colourless crystalline plates melting between 60° and 70°, and have prepared and described several of its salts. Both the acid and its salts, $AgC_2H_3N_2O_3$, $NH_4C_2H_3N_2O_3$, &c., are unstable, and are liable to explode when suddenly heated.

When heated with acids or alkalis, methazonic acid breaks up into *carbon dioxide*, *hydrogen cyanide*, and *hydroxylamine*, according to the equation $C_2H_4N_2O_3 = CO_2 + NH_2OH + HCN$. It is proved that one atom of nitrogen appears as hydrogen cyanide, and the other as hydroxylamine, whilst the carbon is equally divided between the carbon dioxide and the hydrogen cyanide.

On oxidation with permanganate, chromic acid, or hydrogen per-

oxide, methazonic acid furnishes *carbon dioxide*, *hydrogen cyanide*, and *nitric acid*. On reduction either in acid or alkaline solution with weak or strong reducing agents, the principal products are *ammonia* and *formic acid*. No trace of ethylene-diamine or methylamine could be found.

Alkyl derivatives of methazonic acid can be prepared, but they are highly unstable.

The authors propose the formula $HON{:}\overset{\displaystyle H_2C\cdot NH}{\overset{\displaystyle |}{C}}\cdot\overset{\displaystyle |}{\underset{\displaystyle O}{\overset{\displaystyle ||}{O}}}$ for methazonic acid as satisfactorily accounting for its reactions.

Adopting the view of Nef that the "salts" of the nitroparaffins are to be regarded as derived from a tautomeride, and writing the formula of sodium nitromethane as $CH_2{:}\overset{\displaystyle |}{\underset{\displaystyle O}{\overset{\displaystyle ||}{N}}}\cdot ONa$, the authors show how methazonic acid is formed by a process of intermolecular oxidation followed by condensation of the nitromethane residue with formaldoxime simultaneously produced, $2CH_2{:}\overset{\displaystyle |}{\underset{\displaystyle O}{\overset{\displaystyle ||}{N}}}\cdot ONa = NaC_2H_3N_2O_3 + NaOH$.

By a similar process of intermolecular oxidation, followed by condensation with an oxime, it is shown how trimethylisoxazole, acetonitrile, and sodium nitrite are formed by the action of alkalis on nitroethane and how triethylisoxazole and similar products result from the action of alkalis on primary nitropropane; also, how secondary nitropropane gives no isoxazole, but acetone, nitrite, and hydroxylamine.

In this discussion it is assumed that nitro-compounds may be reduced to oximes (Dunstan and Dymond, *Proc.*, 1894, 139), and grounds are now stated for concluding that whilst the nitroparaffins themselves may be reduced (in acid solution) to substituted hydroxylamines, their salts, when reduced (in alkaline solution), furnish oximes or their decomposition products. These facts afford further justification for the view that the "salts" of the nitroparaffins are derivatives of a tautomeride containing the group $\overset{\displaystyle |}{\underset{\displaystyle O}{\overset{\displaystyle ||}{N}}}\cdot OH$.

***133. "Hexachlorides of benzonitrile, benzamide and benzoic acid." By Francis Edward Matthews.**

Benzonitrile mixed with water is saturated with chlorine and exposed to light till the yellow colour of the chlorine disappears. This process is repeated four or five times. The mixture is then subjected to steam distillation till all the benzonitrile has passed over. A thick oil remains which, on purification by solution in, and subsequent

recrystallisation from, glacial acetic acid, gives colourless crystals of benzonitrile hexachloride, $C_6H_5Cl_6 \cdot CN$, melting at 157°.

The hexachloride is not easily hydrolysed, but heating with strong sulphuric acid at 170—180° converts it into the hexachloride of benzamide.

This, crystallised from acetic acid, melts at 187—188°.

On treating the hexachloride of benzamide with fuming nitric acid, the following change takes place: $C_6H_5Cl_6 \cdot CONH_2 + HNO_3 = C_6H_5Cl_6 \cdot CO_2H + N_2O + H_2O$.

The hexachloride of benzoic acid has been obtained pure and has been analysed.

Its most striking property is the decomposition it undergoes on boiling with water, thus: $C_6H_5Cl_6 \cdot CO_2H = C_6H_5Cl_5 + HCl + CO_2$.

The benzoic acid hexachloride and the monochlorobenzenetetrachloride are being further investigated.

***134. "The influence of solvents on the rotation of optically active compounds. I." By T. S. Patterson.**

Experiments to determine the influence of some solvents on the rotation of ethyl tartrate at various concentrations and temperatures were described. From the data obtained it is possible to deduce the rotation in each of the solvents dealt with, at any temperature within the limits of the experiments and at any concentration whatever, with fair accuracy.

The results obtained may be summarised thus:

1. *Water.*—Ethyl tartrate in dilute aqueous solution has a much higher specific rotation than in the pure state. In solutions weaker than 55 per cent. the rotation diminishes with increase of temperature.

2. *Methyl Alcohol.*—In dilute solution in methyl alcohol the specific rotation of ethyl tartrate is considerably higher than in the pure state.

In all solutions the specific rotation increases with increase of temperature, and at much the same rate as that of the pure ester.

3. *Ethyl Alcohol.*—Dilute solutions of ethyl tartrate in ethyl alcohol have a specific rotation slightly higher than that of the pure ester.

A maximum value of the specific rotation only seems to be reached at infinite dilution.

Increase of temperature causes increase of rotation in all solutions, the rate of variation being much the same as in the pure ester.

4. *Propyl Alcohol.*—No mixture of ethyl tartrate and propyl alcohol seems to have a higher specific rotation than pure ethyl tartrate at temperatures below 30°. At higher temperatures this is not the case.

The specific rotation in all solutions increases with increase of

temperature, the rate of increase being generally slightly greater than in the pure ester.

5. *Glycerine.*—Dilute solutions of ethyl tartrate in glycerine have a considerably higher specific rotation at low temperatures than the pure ester, but as in the case of ethyl alcohol, the maximum rotation appears to be reached only at infinite dilution.

The influence of increase of temperature is in all cases to increase the rotation, the rate of increase being in dilute solutions less and in concentrated solutions greater than for the pure ester.

The data obtained were then discussed in order to trace, if possible, the variation in rotation of the dissolved ethyl tartrate to some known property of the solvent. It was suggested that the property known as internal pressure possesses the necessary qualifications, and investigation seems to justify its choice. Since the data obtained render the calculation of molecular solution volume possible, this was first compared with the rotation, and it was shown that a regularity can be established, and that the variation of rotation with change of temperature may be explained by certain assumptions regarding the variation of the asymmetry of a molecule with the variation of its volume.

These phenomena of rotation were then traced back a step further to internal pressure, or what is probably the same thing—heat of disgregation, when very similar regularities are observed, which seems to show that the original assumptions, regarding the dependence of solution volume on internal pressure and of rotation on both, are justified.

***135. "The action of heat on ethyl sulphuric acid." By William Ramsay and G. Rudorf.**

Ethyl hydrogen sulphate, when heated, yields as gaseous products of decomposition, sulphur dioxide, carbon dioxide and monoxide, and ethylene. The oxides of carbon, after the reaction has fairly started, are present in approximately equivalent proportions; this seems to point to the oxidation of the alcohol to oxalic acid, which is at once decomposed by the sulphuric acid. But glycol, heated with sulphuric acid, yields no carbon monoxide, hence this explanation is of questionable validity. When ethylene is bubbled through hot sulphuric acid, the products are the same in kind, and approximately the same in relative amount, as when hydrogen ethyl sulphate is heated. It was proved, in conclusion, that even at 250° carbon monoxide does not deprive sulphuric acid of oxygen; hence the formation of carbon dioxide in the preceding experiments cannot be attributed to the oxidation of carbon monoxide; it must have been a direct product of the reaction.

***136. "Contributions to the knowledge of fluorescent substances. I. The nitro-derivatives of fluorescein." By J. T. Hewitt and B. W. Perkins.**

Attention has been called to the non-fluorescence of the alkaline salts of tetranitrofluorescein (R. Meyer, *Zeit. phys. Chem.*, 1897, **24**, 468; and Hewitt, *Proc.*, 1900, **16**, 3; and *Zeit. phys. Chem.*, 1900, **34**, 1). This absence of fluorescence might possibly be explained by the existence of such tautomerism between the hydroxyl and nitro-groups as usually occurs with ortho- and para-nitrophenols, which would inhibit the double symmetrical tautomerism which, as one of the authors has previously pointed out, is so characteristic of many fluorescent substances. Under these circumstances it seemed very desirable to subject dinitrofluorescein to a further study, since this substance has only been analysed as a hydrate, $C_{20}H_{12}(NO_2)_2O_6$ (von Baeyer, *Annalen*, 1876, **183**, 32). In order to obtain the true anhydrous dinitrofluorescein, its diacetyl derivative, which may be prepared by the action of acetic anhydride on the hydrate, was hydrolysed with fairly concentrated sulphuric acid (80 per cent.). The anhydrous compound thus obtained dissolves in cold dilute soda solution with an orange-brown colour and with no trace of fluorescence. On warming, the solution readily goes blue, a salt of the hydrate being produced.

To determine the position of the nitro-groups in dinitrofluorescein, potash fusion was resorted to, and a small quantity of a substance of m. p. 114° (uncorr.) obtained. Nitroresorcinol ($OH:OH:NO_2 = 1:3:4$) melts at 115°.

Tetranitrofluorescein has also been examined, but the authors have been unable to obtain von Baeyer's numbers on analysis, the results always pointing to the formula $C_{20}H_{10}(NO_2)_4O_6$. Hence arguments deduced from the non-fluorescence of alkaline salts of this compound have no bearing on the question as to whether a pyrone ring is a "fluorophor" as the pyrone ring does not exist in the compound. Hence the results obtained with regard to the non-fluorescence of the alkaline solutions of dinitrofluorescein are especially significant, since in this compound the pyrone ring may be preserved intact and the fluorescence inhibited by the nitro-groups alone.

137. "Derivatives of ethyl α-methyl-β-phenylcyanglutarate." By W. Carter and W. Trevor Lawrence.

When ethyl cinnamate and ethyl sodiocyanacetate are allowed to interact in alcoholic solution, methyl iodide being subsequently added to the condensation product, it is found that the neutral reaction

mixture consists almost entirely of equal quantities of the two stereoisomeric forms of ethyl α-methyl-β-phenyl-α-cyanglutarate, $C(CO_2Et)(CH_3)(CN)\cdot CH(C_6H_5)\cdot CH_2(CO_2Et)$.

The α-modification is a crystalline solid, crystallising from ligroin in prisms which melt at 89°, the β-modification is a liquid boiling at 260° (100 mm.); both isomerides, on addition of alcoholic potash, are converted into microcrystalline potassium salts, which separate completely from the mother liquor.

From these potassium salts two distinct acids are obtained. The α-acid is fairly soluble in water, from which it separates slowly in prisms, melting with decomposition at 161°; the β-acid is much less soluble in water and melts at 194°.

Both acids are converted by hydrochloric acid into methyl-phenyl-glutarimide, $\begin{matrix} CO & \text{———} & NH & \text{———} & CO \\ | & & & & | \\ CH(CH_3)\cdot & & CH(C_6H_5)\cdot & & CH_2 \end{matrix}$ (prisms from water, m. p. 144°), and are completely hydrolysed by sulphuric acid with formation of methyl-phenyl-glutaric acid; on prolonged boiling with aqueous potash, they are converted into α-methyl-β-phenyl-αα-γ-propanetricarboxylic acid, $C(CO_2H)_2(CH_3)\cdot CH(C_6H_5)\cdot CH_2(CO_2\cdot H)$, which crystallises from a mixture of chloroform and acetone, and melts, with decomposition, at 148°.

Acetyl chloride offers a means of differentiating between the two modifications, as it converts the α-acid into a substance melting at 110°, which possesses acid properties, and is easily decomposed by water, whereas the β-acid forms a neutral substance melting at 146°, which is fairly stable towards water. The following formulæ have been assigned to the α- and β-esters, acids, and acetyl derivatives:

	α-.	β-.
Esters	$CO_2Et\cdot C(CH_3)\cdot CN$ $\quad\quad\quad

By this reaction methylphenylglutaric acid, previously obtained with great difficulty (Avery and Fossler, *Am. Chem. J.*, 1899, **20**, 516), may be easily prepared.

α-Methyl-β-phenylglutaric acid, $CH(CH_3)(CO_2H)\cdot CH(C_6H_5)\cdot CH_2(CO_2H)$ crystallises from water or ligroin in prisms (m. p. 125°); theoretically, the acid should exist in two modifications, but up to the present time the authors have only isolated one form, which, from its easy conversion into the anhydride, is probably the *cis*-modification.

Acetyl chloride converts the acid into a double anhydride with acetic acid, which crystallises from benzene in asbestos-like masses, melting at 107°; its formula is $[C(CO\cdot O\cdot COCH_3)H(CH_3)\cdot CHC_6H_5\cdot CH_2\cdot CO]_2O$. When this is distilled, the true anhydride of methylphenylglutaric acid is obtained as a gum which slowly solidifies to a solid mass melting at 74°; the corresponding anilic acid is also a gum.

Methylphenylglutaric acid is unacted upon by boiling permanganate solution; boiling with fuming nitric acid converts it into two nitro-derivatives, of which the less soluble melts at 208° and the more soluble at 179°; both substances possess the formula $C_{12}H_{13}O_4\cdot NO_2$, and are probably *o*- and *p*-nitrophenylmethylglutaric acid.

138. **"The nitration of acetamino-orthophenyl acetate (diacetylorthoaminophenol). A correction." By Raphael Meldola, F.R.S., and Elkan Wechsler.**

The object of this note is to correct and extend the statement (Meldola, Woolcott, and Wray, *Trans.*, 1896, **69**, 1325) that the nitration of acetamino-orthophenol acetate under the conditions specified gave a mononitro-derivative, which, on further nitration, gave a dinitro-derivative. A repetition of this work has led to the conclusion that a dinitro-derivative is produced under all conditions of nitration. The statement in the paper above referred to was based on an error of analysis. The dinitro-derivative crystallises from hot water in long, ochreous needles melting at 201°, and softening at a temperature some degrees lower.

Two experiments gave N = 17·30 and 17·39 per cent. respectively. $C_6H_2(NO_2)_2\cdot NHAc\cdot OH$ requires N = 17·42 per cent.

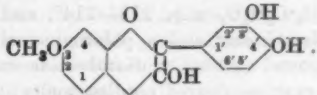
One acetyl group is split off during nitration. The dinitro-derivative is readily hydrolysed by boiling for a short time with sodium hydroxide solution, and the dinitro-aminophenol thus obtained proved to be *picramic acid* as shown by the melting point (167—168°), by conversion, by the diazo-method, into 2-chloro-4 : 6-dinitrophenol of m. p. 110—111°, and by a comparison of the properties of the diazoxide with the description of this compound given by Griess (*Annalen*, **113**, 205).

The nitration of diacetyl orthoaminophenol thus gives rise to the

direct formation of 2-acetamino-4 : 6-dinitrophenol, and the formulæ given in that section of the previous paper must be revised accordingly.

139. "Rhamnazin and rhamnetin." By A. G. Perkin and J. R. Allison.

In rhamnazin (quercetin dimethyl ether), the position of but one methoxyl group is known (*Trans.*, 1897, '71, 818), whereas that in rhamnetin (quercetin monomethyl ether) (Herzig, *Monatsh.*, 1888, **9**, 548) has not been determined with certainty. On gentle decomposition, rhamnazin, rhamnetin and quercetin tetramethyl ether give the same phloroglucinol derivative, as in each case the latter reacts with diazobenzene to form a compound, occurring in orange-red needles, m.p. 251—252°. This is *diazobenzenephloroglucinol monomethylether*. (Found C = 65·17 ; H = 4·64 ; N = 15·57 ; CH_3 = 4·40 per cent.) ; consequently rhamnazin is methoxyrhamnetin, and both contain a methoxyl group in the (3) position.



Rhamnetin.

140. "Luteolin. III." By A. G. Perkin and L. H. Horsfall.

On methylation, luteolin (from weld) yields two ethers insoluble in alkali, (*a*), m. p. 191—192° (*Trans.*, 1896, **69**, 206) and a more soluble compound (*b*), newly isolated, m. p. 161—163°. The latter, $C_{15}H_7O_8(OCH_3)_3$, is the true *luteolin trimethyl ether*, for on decomposition it forms *veratric acid* and *phloroglucinol monomethyl ether* (identified as its diazobenzene derivative, m. p. 251—252°). The ether (*a*), m. p. 191—192°, appears to be *methylluteolin trimethyl ether*, due to the existence of a methyl group entering the ring during methylation, or less probably to the presence of methylluteolin in weld. On gentle decomposition, *veratric acid*, and a crystalline phloroglucinol derivative result, the latter yielding, with diazobenzene, a derivative, in orange-coloured needles, m. p. 198—200°, $C_8H_8O_7(C_6H_5N_2)_2$, apparently *diazobenzenemethyl phloroglucinol monomethyl ether*. *Acetyl methylluteolin*, colourless needles, melts when rapidly heated at 238—240°. Luteolin from the *Genista tinctoria* behaves similarly on methylation. The monopotassium and sodium salts of luteolin have now been crystallised, and have the respective compositions $KC_{15}H_9O_6$ and $NaC_{30}H_{19}O_{12}$. Weld contains a trace of another colouring

matter, $C_{15}H_{10}O_8$, which, on decomposition with alkali, yielded *p-hydroxybenzoic acid*, a trace of protocatechuic acid, *phloroglucinol*, and *p-hydroxyacetophenone*. By further reactions, it was identified as *apigenin*. By the gentle action of alkali, morin, a colouring matter of *Morus tinctoria*, yields, in addition to *β*-resorcylic acid and phloroglucinol (*Trans.*, 1896, **69**, 697), previously found, some quantity of *β-resorcylic aldehyde*.

141. "Genistein. II." By A. G. Perkin and L. H. Horsfall.

Genistein dimethyl ether m.p. 137—139° (*Trans.*, 1899, **75**, 835) yields a monacetyl derivative m.p. 202—204°, $C_{14}H_7O_2(OCH_3)_2C_2H_3O$, and on gentle decomposition gives *p-methoxyphenylacetic acid* and *phloroglucinolmonomethyl ether*, identified as its diazobenzene derivative m.p. 251—252°. The second product of the methylation, m.p. 200—202° (previously given as 187—189°), appears to be a *methylgenistein dimethyl ether* (compare luteolin). It forms a monacetyl derivative, $C_{17}H_{15}O_5 \cdot C_2H_3O$, m.p. 212—214°, and on decomposition gives *methoxyphenylacetic acid* and a phloroglucinol derivative whose diazobenzene compound (probably *diazobenzene methylphloroglucinolmonomethyl ether*), orange-coloured needles, melts at 198—200°. This is identical with that produced from methylluteolintrimethyl ether. *Genistein diethyl ether*, $C_{14}H_8O_3(OEt)_2$, colourless needles, m.p. 132—134°, and its monacetyl derivative, m.p. 168—170°, have been obtained. On decomposition it gives *p-ethoxyphenylacetic acid* and a phloroglucinol compound. These results are in harmony with the constitution of a *trihydroxyphenylketocumaran* previously suggested (*loc. cit.*) for genistein. Genistein from *Genista tinctoria* melts at 291—293°.

142. "The colouring matter of the flowers of *Delphinium consolida*." By A. G. Perkin and E. J. Wilkinson.

The presence of a yellow colouring matter in these flowers (in the form of glucoside) has been previously notified (*Trans.*, 1898, **73**, 275). This compound forms yellow needles, has the composition $C_{15}H_{10}O_6$ (found C = 62·85; H = 3·63 per cent.), and on fusion with alkali gives phloroglucinol and *p*-hydroxybenzoic acid (found C = 60·71; H = 3·94). The *tetracetyl* compound, $C_{15}H_6O_6(C_2H_3O)_4$ (found C = 60·64; H = 4·17), is peculiar, for when crystallised from alcohol it melts at about 114—116°, resolidifies at a higher temperature, and again melts at 181—183°. This is not due to alcohol of crystallisation. The *sulphate*, $C_{15}H_{10}O_6,H_2SO_4$, orange-red needles (found C = 46·71; H = 3·39), the *hydriodide*, $C_{15}H_{10}O_6HI$ (found

C = 44·25; H = 3·00), and the *monopotassium* salt, $C_{15}H_9O_6K$ (found K = 11·85), have been obtained, but are less stable than is usually the case with such compounds. The colouring matter has properties resembling those assigned to kampherol (Gordin, *Diss. Berne*, 1897), obtained by the decomposition of its methyl ether, kampherid, which exists in galanga root (*Alpinia officinarum*). The investigation will be continued with the hope of ascertaining the identity of this colouring matter with certainty.

143. "Note on Gallinek's amidomethylnaphthimidazole." By Raphael Meldola, F.R.S., and Frederick William Streatfeild.

A paper by Gallinek has just been published (*Ber.*, 1900, **33**, 2315) on a sulphonic acid of the anhydro-base obtained by reducing dinitro-*a*-acetnaphthalide. Gallinek assumes that the base he has been dealing with is the same as that described by the authors (*Trans.*, 1887, **51**, 691), and he considers that their failure to separate the base in the free state was due to their having had impure dinitro-*a*-acetnaphthalide as their raw material. The authors desire now to point out that Gallinek is completely in error in his original assumption, and that the base described by him is isomeric, and not identical with that described by the authors in 1887. Gallinek does not state what reducing agent he employed, nor does he refer to the process published by Markfeldt (*Ber.*, 1898, **31**, 1174), but his description of the base as being stable, solid and crystallisable from water renders it tolerably certain that he has been investigating Markfeldt's base. Markfeldt also assumed that his base was identical with that described by the authors in 1887. The isomerism was recently made known and the properties of the base obtained by Markfeldt's process somewhat fully characterised (Meldola and Eynon, *Trans.*, 1900, **77**, 1159). The authors think it necessary to indicate the true cause of the apparent discrepancy between the statements of the German investigators and themselves, because they are at present engaged in the further investigation of the nature of the isomerism.

144. "The amount of chlorine in rain water collected at Cirencester." By Edward Kinch.

The author has already published the results (*Trans.*, 1887, **51**, 92) of the estimation of the chlorine in the water collected in a rain gauge at the Royal Agricultural College, 443 feet above sea level, and about 35 miles distant from the sea. The results of his determinations up to the present time are summarised below.

The rain water for periods of six months, namely, summer months, April to September, and winter months, October to March, inclusive, gave the following averages:

Periods.	Rainfall in inches.	Chlorine per million.	Equivalent to NaCl, grams per gallon.	Equivalent to NaCl, lbs. per acre.
Mean of 14 winter periods to March, 1900	14·26	3·55	0·412	19·35
Mean of 14 summer periods to September, 1900	12·78	2·27	0·261	10·40
Average of 14 years to September, 1900	27·04	2·91	0·337	29·75
Mean of 26 winter periods to March, 1900	15·83	3·76	0·435	21·29
Mean of 26 summer periods to September, 1900	14·78	2·58	0·302	14·81
Average of 26 years to September 31st, 1900	30·61	3·17	0·369	36·10

145. "Researches on the alkyl-substituted succinic acids. III. Dissociation constants." By W. A. Bone and C. H. G. Sprankling.

The authors have prepared, and determined the dissociation constants of, a number of new alkyl-substituted succinic acids as follows:

		M. p.	*K*.
sym-Di-*iso*butylsuccinic	*trans*-	195°	0·0225
	cis- ...	97— 98	0·056
$\alpha\alpha_1$-Methylpropylsuccinic	*trans*-	158—160	0·0355
	cis- ...	92— 93	0·0271
$\alpha\alpha_1$-Methyl*iso*butylsuccinic	*trans*-	133	0·0427
	cis- ...	89— 90	0·0236
$\alpha\alpha_1$-Methyl*iso*amylsuccinic.....	*trans*-	141—142	0·0236
	cis- ...	93	0·0385
$\alpha\alpha$-Dimethyl-α_1-ethylsuccinic		139—140	0·0566
$\alpha\alpha$-Dimethyl-α_1-propylsuccinic.....		145	0·060
$\alpha\alpha$-Dimethyl-α_1-*iso*propylsuccinic		141—142	0·0158
$\alpha\alpha$-Dimethyl-α_1-*iso*butylsuccinic.....		143—144	0·0432
$\alpha\alpha$-Dimethyl-α_1-*iso*amylsuccinic		143—144	0·0616

They then discuss, in the light of the above and previous results, the effect of alkyl-substitution on the magnitude of the dissociation constant of a succinic acid, and deduce the following conclusions.

Each alkyl group exerts its own influence upon the constant dependent on its mass and structure. In the case of *normal* radicles, where the influence of 'mass' only is to be traced, an increase in the mass of the alkyl is invariably accompanied by a corresponding rise in the constant. In the case of 'iso'-radicles, there is, however, a 'structural' effect opposed to that of mass, except in the case of the

cis-aa_1-substituted acids, which are separately discussed; the magnitude of this structural effect is always dependent on the proximity of the 'iso'-linkage to the carbon atom to which the carboxyl group is attached.

146. "The reaction between ethyl alcohol and hydrochloric acid." By T. Slater Price, D.Sc.

The present investigation was undertaken in order to measure the velocity of reaction between hydrochloric acid and ethyl alcohol. On redetermining the equilibrium constants it was found that they varied with the amount of acid used. (The constants (a) were calculated according to the equation $a=(A-x)(B-x)/(C+x)(D+x)$ where A, B, C, and D are the concentrations of the alcohol, acid, water and ester respectively at the commencement of the reaction, and x the amount of fresh ester formed when equilibrium is reached.) The results obtained agree with those of Zaitschek (*Zeit. phys. Chem.*, 1897, 24, 1), who investigated the action of sulphuric acid on alcohol.

Determinations were made at 77°, 99° and 129·5°. The value of a decreases as the amount of acid increases; this is well shown especially in the experiments at 77°, as the lower the temperature the greater is the variation.

The results obtained by the author are found to agree very well with the equation $dx/d\theta=k_1(A-x)(B-x)^2-k_2(C+x)(D+x)(B-x)$, where k_1 and k_2 are the velocity constants of the direct and reverse reactions, x is the amount of ester formed after the time θ, and A, B, C, and D have the signification given above. The catalytic effect of the hydrogen ions is assumed to be proportional to the amount $(B-x)$ of acid present, this holding good over a short interval of time, and since both the direct and reverse reactions are affected the factor $(B-x)$ will be extra in each term of the velocity equation. The values of k_1 so obtained are especially good when no water is present to begin with, that is, when $C=0$ (in no case was ester present at the commencement of the reaction), but when the reaction mixture used contained water to start with, the values of k_1 diminish as θ increases.

The value of k_1 decreases as the concentration of the acid increases, and is also greatly diminished when water is present.

The velocity of reaction increases very rapidly with the temperature, the increase being much greater than in the case of the action of organic acids on alcohol.

ADDITIONS TO THE LIBRARY.

I. Donations.

Bartley, D. C. Adulteration of Food. Statutes and cases dealing with coffee, tea, bread, seeds, food and drugs, margarine, fertilisers and feeding stuffs, &c., including the Food and Drugs Act, 1899. Second edition. London 1899.

Clowes, Frank, and Coleman, J. B. Quantitative chemical analysis. Fifth edition. London 1900. From the Authors.

Duparc, L., Degrange, E., et Monnier, A. Traité de chimie analytique qualitative suivi de Tables systématiques pour l'analyse minérale. Genève et Paris 1900. From Messrs. Sampson, Low and Co.

Letts, E. A., and Blake, R. F. The carbonic anhydride of the atmosphere. (Reprinted from the *Proceedings* of the Royal Dublin Society). Dublin 1900. From the Authors.

Mitchell, C. Ainsworth. Flesh foods, with methods for their chemical, microscopical, and bacteriological examination. London 1900. From the Author.

Roos, L. Wine-making in hot climates. Translated by R. Dubois and W. P. Wilkinson. Melbourne 1900. From the Translators.

Sutton, Francis. A systematic handbook of volumetric analysis. Eighth edition. London 1900. From the Author.

Gerhardt, Charles, sa vie, son œuvre, sa correspondance 1816-1856. Document d'histoire de la chimie, par Edouard Grimaux et Charles Gerhardt. Paris 1900. From the Authors.

Bedford, the Duke of, and Pickering, S. U. Second report on the working and results of the Woburn Experimental Fruit Farm. London 1900. From the Authors.

At the next meeting, on Thursday, November 15th, the following paper will be communicated.

"The bases contained in Scottish shale oil." By F. C. Garrett, M.Sc., and J. A. Smythe, B.Sc., Ph.D.

RICHARD CLAY AND SONS, LIMITED, LONDON AND BUNGAY

Issued 22/11/1900

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 16. No. 228.

November 15th, 1900. Professor THORPE, C.B., F.R.S., President, in the Chair.

Messrs. F. C. Britten, G. C. Thomson, R. G. Halstead, and J. A. Mathews were formally admitted Fellows of the Society.

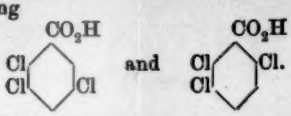
The following certificates were read for the first time:—Messrs. H. H. Cousins, Government Laboratories, Kingston, Jamaica; Robert Dodd, 28, Sibella Road, Clapham, S.W.; Arthur Houldershaw, 71, Lavender Gardens, West Jesmond, Newcastle-on-Tyne; Edward Hughes, Rectory, Barmouth; Robert Salmon Hutton, Owens College, Manchester; Stephen Archigenes Ionides, Balliol College, Oxford; Robert Henry Jones, Glen Albyn, Coity Road, Bridgend, Glam.; H. T. G. van der Linde, 101, Tyndall Avenue, Toronto, Canada; William Meredith, 63, Albion Place, Ulverston; James Moir, The Ash, 62, Hamilton Place, Aberdeen, Scotland; H. M. Smith, 79, Helix Road, Brixton, S.W.

Of the following papers, those marked * were read:—

***147. "Trichlorobenzoic acid." By Francis Edward Matthews.**

The hexachloride of benzonitrile is acted upon by alcoholic sodium hydroxide, forming a mixture of trichlorobenzoic acids, which, on fractional crystallisation of the barium salts, was found to give a new trichlorobenzoic acid.

At present four of the six possible trichlorobenzoic acids are known, the missing two being



As the new acid was found to yield an ester readily when treated with hydrogen chloride and alcohol, which an acid having the second of the above formulæ should not do, both positions adjacent to the carboxyl group being occupied by chlorine, the former of the two formulæ may be taken as proved.

By the action of quinoline upon the nitrile, $C_6H_5Cl_6\cdot CN$, followed by steam distillation, the nitrile of the new acid, $C_6H_2Cl_3\cdot CN$, is easily prepared in a state of purity. It crystallises from aqueous alcohol in long, white, lustrous needles melting at 87°. After hydrolysis with alcoholic sodium hydroxide, the acid, which crystallises from water in small needles melting at 163°, is readily obtained.

The following salts have been prepared: $(C_6H_2Cl_3CO_2)_2Ba + 3H_2O$; $(C_6H_2Cl_3\cdot CO_2)_2Sr + 3H_2O$; $(C_6H_2Cl_3\cdot CO_2)_2Ca + 4H_2O$; $C_6H_2Cl_3\cdot CO_2Ag$. The acid chloride, $C_6H_2Cl_3\cdot COCl$, melts at 36°; the amide, $C_6H_2Cl_3\cdot CONH_2$, crystallises in small needles which melt at 204—205°.

The ethyl ester, $C_6H_2Cl_3\cdot CO_2Et$, is obtained by the action of hydrogen chloride and alcohol upon the acid. It is a liquid volatile with steam and possessing, but in a lesser degree, the odour of ethyl benzoate.

***148. "Oxidation of benzalthiosemicarbazone." By George Young, Ph.D., and William Eyre, B.Sc.**

Benzal thiosemicarbazone, $C_6H_5\cdot CH{:}N\cdot N{:}C(SH)\cdot NH_2$, is oxidised by ferric chloride to *amidophenylthiodiazole*, $C_6H_5\cdot C<\overset{N\cdot N}{S}>C\cdot NH_2$. The base melts at 222—223°, its hydrochloride at 213—214°. The methyl derivative, $C_6H_5\cdot C_2N_2S\cdot CH_3{:}NH$, is an oil; its platinichloride, $[C_9H_9N_3S]_2H_2PtCl_6$, melts at 218°. The acetyl derivative, $C_6H_5\cdot C_2N_2SNH\cdot COCH_3$, which melts at 276°, is an acid forming stable sodium and silver salts. Both the methyl and acetyl derivatives yield the same methylacetyl derivative, $C_6H_5\cdot C_2N_2SCH_3{:}N\cdot COCH_3$, which melts at 144°.

Benzal-4-methylthiosemicarbazone, $C_6H_5\cdot CH{:}N\cdot N{:}C(SH)\cdot NH\cdot CH_3$, is similarly oxidised to $C_6H_5\cdot C<\overset{N\cdot N}{S}>C\cdot NH\cdot CH_3$, *methylamidophenylthiodiazole*, which melts at 183—184°. Its platinichloride, $[C_9H_9N_3S]_2H_2PtCl_6$, melts at 208—209°. The acetyl derivative, $C_6H_5\cdot C_2N_2S\cdot N<\overset{CH_3}{COCH_3}$, melts at 195°.

Benzal-4-phenylthiosemicarbazone, $C_6H_5 \cdot CH:N \cdot N:C(5H) \cdot NH \cdot C_6H_5$, yields phenylamidophenylthiodiazole, $C_6H_5 \cdot C<\overset{N \cdot N}{S}>C \cdot NH \cdot C_6H_5$, previously described by Marckwald. Its silver derivative, $C_{14}H_{10}N_3SAg$, decomposes with explosive violence when suddenly heated.

***149. "The nitration of benzeneazosalicylic acid." By J. T. Hewitt and J. J. Fox.**

One of the authors has already pointed out (Hewitt, *Trans.*, 1900, 77, 99) that when dilute nitric acid is warmed with benzeneazophenol a substance results in which the nitro-group has entered the phenol nucleus in the ortho-position relatively to the hydroxyl. Noelting, on the other hand, by nitrating benzeneazophenol in strong sulphuric acid obtained paranitrobenzeneazophenol (*Ber.*, 1887, 20, 2997).

The authors have studied the action of nitric acid on benzeneazosalicylic acid under varying conditions and find that with dilute acid at 65—70° the nitro-group enters the salicylic acid residue in the ortho-position relatively to the hydroxyl. The constitution of the resulting compound was determined by comparison with the product obtained from phenyldiazonium chloride and nitrosalicylic acid ($CO_2H : OH : NO_2 = 1 : 2 : 3$).

Benzeneazoorthonitrosalicylic acid melts at 197° (uncorr.), its *methyl ester* at 132—134° and the *ethyl ester* at 128—129°.

By the nitration of benzeneazosalicylic acid dissolved in concentrated sulphuric acid paranitrobenzeneazosalicylic acid, identical with the substance described by Meldola (*Trans.*, 1885, 47, 666), was obtained. Its ethyl ester melts at 220—225°.

***150. "Upon the collection and examination of the gases produced by bacteria from certain media." By Walter C. C. Pakes and Walter H. Jollyman.**

The authors described a new apparatus for the collection of the gases produced by bacteria when grown either under ærobic or anærobic conditions.

Experimenting with the *Bacillus pyocyaneus*, which is supposed to be a strictly ærobic organism, they found that it grew in media containing 1 per cent. of potassium or ammonium nitrate under the strictest anærobic conditions as the term is at present understood (that is, in the presence of hydrogen, or in the absence of any gas). They concluded, therefore, that the terms ærobic and anærobic must be extended to include the presence of oxygen in the form of nitrates.

Upon analysing the gases produced by this organism from media containing nitrates, they found that both free oxygen and free nitrogen were evolved, the former in small quantities but constantly.

151. "The bases contained in Scottish shale oil." By Frederic Charles Garrett, M.Sc., and John Armstrong Smythe, B.Sc., Ph.D.

Though many investigators have examined the bases contained in coal tar, but little attention has been paid to those present in shale oil, the authors have therefore undertaken the examination of those obtained from the Broxburn oil. The shale, on distillation, yields gas, ammonia water and "crude oil"; this "crude oil" is again distilled, giving "green naphtha," "green oil" and "still coke," the temperature towards the end of the operation rising to a red heat. A quantity of this "green naphtha" was washed with ¼ per cent. of sulphuric acid (diluted to about 15 per cent.). Steam was blown through the reddish-brown liquid so obtained for several hours to free it from a small quantity (about 0·1 per cent.) of an oily liquid possessing a peculiarly disgusting smell; when this had been removed sodium hydroxide solution (17½ per cent.) was added and superheated steam blown through until all the volatile bases had been driven over. The soluble bases in the distillate were thrown out by the addition of solid sodium hydroxide, the mixed bases were then dried by solid potash and fractionally distilled; each litre of the crude acid liquor yields about 120 grams of the dry bases, of which about 25 per cent. boil below 170°, and 46 per cent. between 170° and 205°.

The basic oil thus obtained was then repeatedly refractionated, and an attempt made to isolate the various bases in the lower fractions by precipitation with mercuric chloride and fractional crystallisation of the salts so obtained. The portion boiling below 125° (about 10 grams) was examined for pyridine by precipitation with potassium ferrocyanide but none was found, the base being chiefly α-picoline (b. p. 128°); from the other fractions below 160°, the symmetrical collidine (αγα′-trimethyl pyridine) and two other bases which appear to be the hitherto undescribed lutidines (αβ- and αβ′-dimethyl pyridine). The first of these boils at about 160° and yields a platinichloride melting with decomposition at 208°, whilst the second boils at about 140°, and although no platinum compound was isolated it yielded a gold compound melting at 73°; in each case, however, the amount of base obtained was very small. Having now obtained between two and three kilograms of the raw bases, the authors are attempting a more systematic examination of them.

The authors have to thank Mr. George Beilby for calling their

attention to the necessity for this work, and Mr. D. R. Steuart for kindly providing them with the raw material they required.

152. "On a simplified method for the spectrographic analysis of minerals." By Walter Noel Hartley, F.R.S., and Hugh Ramage, A.R.C.Sc.I.

The authors pointed out that some of the rare earths are very difficult to detect and others more widely diffused are not easily separated and recognised either by the ordinary methods of chemical analysis or by spectroscopic examination. A simplification of the method of obtaining oxyhydrogen blow-pipe spectra (Hartley, *Phil. Trans.*, 1894, 185, 168) was described and examples given of its application to the analysis of various metallurgical products, metallic ores, and siliceous minerals. The method is to burn the metals, minerals, or precipitates on ashless filter papers in an oxyhydrogen flame and to photograph the spectra in the usual way. Refractory silicates in very fine powder are decomposed by being heated with strong sulphuric acid and ammonium fluoride which has been purified by distillation in a platinum retort. After the complete decomposition of the mineral the sparingly soluble sulphates are separated by filtration and burnt on the ashless paper. The hydroxides of the heavy metals are precipitated by ammonia and similarly burnt. The alkalis are contained in the aqueous solution of which the treatment is varied according to the nature of the substance under examination. For the separation of rubidium and cæsium, platinic chloride is used and the platinichlorides collected and burnt.

ADDITIONS TO THE LIBRARY.

By Purchase.

Cohnheim, Otto. Chemie der Eiweisskörper. Braunschweig 1900.

Migula, W. System der Bakterien. Handbuch der Morphologie, Entwickelungsgeschichte und Systematik der Bakterien. Vol. I. Allgemeiner Teil. Vol. II. Specialle Systematik der Bakterien. Ill. Jena 1900.

Minet, Adolphe. Traité théorique et pratique d'électro-chimie. Ill. Paris 1900.

Pictet, Amé. Die Pflanzenalkaloïde und ihre chemische Konstitution. Second German edition by Richard Wolffenstein. Berlin 1900.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE NEXT BALLOT.

The following Candidates have been proposed for election. A ballot will be held on Thursday, December 6th, 1900.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

Bennett, George Lowe,

13, St. Domingo Vale, Everton, Liverpool.

Clerk in Holy Orders. Student of Chemistry, Oxford University, for over three years. Graduated from St. John's College in the Honours School of Chemistry, 1898. Was Casberd Exhibitioner in Chemistry (St. John's College, 1896). Have been Lecturer in Chemistry in Organised Science School.

W. W. Fisher. J. E. Marsh.
P. Elford. *V. H. Veley.*
John Watts.

Binks, Frederick Nisbet,

2, Hollywell Terrace, Millbourne Avenue, Drumcondra, Dublin.

Analytical Chemist. Three years' training in the "Young" Laboratories of the Glasgow and West of Scotland Technical College; 10½ years Assistant to Professor Tichborne, Dublin. Lecturer on Theoretical Chemistry to the Pharmaceutical Society of Ireland, and on Practical Chemistry in the Pembroke Technical Schools.

Chr. R. C. Tichborne. Geo. Ritchie.
Edmund J. Mills. *R. R. Tatlock.*
J. Anderson Craw.

Boyes, Herbert James Singleton,

9, Rua Episcopal, São Paulo, Brazil.

Analytical Chemist. I have been a Student in Owens College, Manchester, taking private course in Chemistry for two years, and have been with Dr. Burghardt, Analytical Chemist, 35, Fountain Street, Manchester, eight months. I am now going abroad as an Analytical Chemist

H. B. Dixon. George J. Allen.
J. R. Appleyard. *W. S. Spencer.*
Walter Ratcliffe.

Burnett, Theodore Ridley,

83, Coltart Road, Liverpool.

Analytical Chemist. At present Assistant in the Laboratory of Professor J. Campbell Brown, D.Sc., Analyst for the County of Lancaster, &c. Studied Chemistry as chief subject for degree of B.Sc. (Vict.) at University College, Liverpool, 1894—1898. Studied at the Polytechnikum, Zürich, under Professors Lunge and Treadwell (1898—1900) for the degree of Ph.D., which was taken at Basel University. Thesis for this degree, "Ueber die Bestimmung der Halogene neben einander."

W. Collingwood Williams. J. Campbell Brown.
H. B. Stocks. Charles A. Kohn.

Edwin Dowzard.

Cheeseright, John Henry,

80, Sydney Road, Hornsey, N.

Science Teacher. Honours in Chemistry and Electricity and Qualified Teacher of Chemistry (Science and Art Department). Intermediate Science, London University.

W. Ball. J. W. Shepherd.
Edward Masters. W. M. Bailey.

John J. Pilley.

Comber, Albert Walter,

Rio Marina, I. d'Elba, Italy.

Metallurgical Chemist. Diploma in Chemistry, Finsbury Technical College (1894—1897). Intermediate Exam. of the Institute of Chemistry (1899). I was for one year (1898) assistant to W. A. Shenstone, Esq., F.R.S., of Clifton College. I was for seven months (Jan.—Aug., 1899) with E. Riley, Esq., F.C.S., F.I.C., of London, for whom I have been acting since Aug., 1899, as sole chemist to the Royal Mines of Elba.

Raphael Meldola. Edward Riley.
W. A. Shenstone. Robt. D. Connell.

James E. Ferguson.

Davidson, Alexander, jun.,

1 Almond Bank Terrace, North Merchiston, Edinburgh.

Chemist to J. and G. Cox, Ltd., Gorgie Mills, Edinburgh. Studied chemistry for six years at the Glasgow Technical College. Elected an "Associate of the Glasgow Technical College" in 1898. Elected an "Associate of the Institute of Chemistry" in 1900. Engaged in

research work with Prof. G. G. Henderson during session 1898—99 and part of session 1899—1900.

G. G. Henderson. James Robson.
Thomas Gray. Matthew A. Parker.
D. S. Jordan.

Fechtner, Arthur Louis William,
186, Spring Bank, Hull.

Manufacturing and Analytical Chemist. Qualified by examinations of the Pharmaceutical Society of Great Britain; for four years Managing Manufacturing and Analytical Chemist to the English Pharmacy, Cairo, Egypt, and for seven years (and at present) in the above capacity at the above address.

Jas. Baynes. Fras. A. Drake.
Harry Thompson. *Frederic Wm. Richardson.*
S. Hill.

Freeman, Willie Ludford, B.A.,
102, Marlboro'-road, Oxford.

Schoolmaster. Final Honours in the School of Natural Science (Chemistry), Oxford, 1900.

William Odling. J. E. Marsh.
W. W. Fisher. C. H. H. Walker.
V. H. Veley. *P. Elford.*

Gasson, William,
Kimberley, South Africa.

Chemist and Analyst. Studied Chemistry and other Branches of Science connected with Pharmacy and passed examinations of the Pharmaceutical Society of Great Britain. During past ten years as Analytical Chemist and Assayer in Kimberley, South Africa. Well versed in Metallurgical Processes. The Governor of the Colony has recognised my services by granting a special appointment as Analyst. Desirous of being connected with the Society in order to be in touch with those interested in similar pursuits in England.

M. Carteighe. *Edwin Dowzard.*
W. A. H. Naylor. *Edward Davies.*
Peter MacEwan. *Ernest J. Parry.*

Gibbings, George William,
Standard Bank of S. Africa, Ltd., Salisbury, Mashonaland.

Assayer. Studied Chemistry at Exeter Technical College under Mr. Clayden. Hold Science and Art Advanced Certificates. Three years Chemist in Soapworks, Exeter. Assistant Assayer at Standard Bank

Assay Office, Johannesburg. Assistant Assayer at Standard Bank Assay Office, Bulawayo, Rhodesia. At present the Assayer to the Standard Bank, Salisbury, Rhodesia.

L. Ludlow. Geo. A. Pingstone.
Gerald A. Parker. Arthur W. Clayden.

W. H. Lewis.

Gibson, John,

Battle Hill, Hexham, Northumberland.

Chemist. Studied analytical Chemistry for three years under Mr. G. F. Merson, F.C.S. Engaged in Chemistry as specially applied to Photographic Processes, and desirous to obtain the Society's Journal.

Fredk. Gilderdale. *W. A. H. Naylor.*
E. D. Walrond. *Geo. Bult Francis.*
Frank R. Dudderidge. *Charles H. Bothamley.*
Geo. F. Merson. *P. Phillips Bedson.*

Handcock, Walter Augustus,

Southbank, 40, Avenue Road, Highgate, London, N.

Student. Certificated Chemical Student of The City and Guilds Technical College, Finsbury. Educated at University College School. Matriculated Student, London University.

R. Meldola. F. Southerden.
Gerald T. Moody. W. A. Davis.

T. M. Lowry.

Hargreaves, William Arthur,

Port Adelaide, South Australia.

Government Analyst and Inspector of Explosives to the Government of South Australia. Government Analyst under Food and Drugs Act, Fertilisers Act, and other Acts. Analyst to H.M, Customs, and to the Marine Board of South Australia. Formerly First Assistant Government Analyst in the Colony of Queensland, also Lecturer on Chemistry to the College of Pharmacy, Queensland. Is Master of Arts and Bachelor of Civil Engineering of the University of Melbourne, where he graduated first in the first class at the fina honour examinations in the School of Natural Science.

J. C. Brünnich. A. Alexander Ramsay.
G. A. Goyder. Edward H. Rennie.

W. F. Butcher.

Harker, George,

35, Boulevarde, Petersham, Sydney, N.S.W.

Student. B.Sc. in Chemistry (1st Class Honours), 1899. Junior Demonstrator in Chemistry, University of Sydney, from September, 1898, to June, 1899. *Research Work.* "On the Composition of

N.S.W. Labradorite and Topazes, with a Comparison of Methods for the Estimation of Fluorine," *Journ. Roy. Soc. N.S.W.*, 1899. Two papers "On the Alkaloids of Australian Plants," and "On the Estimation of Nicotine and on the Amount of Nicotine in N.S.W. Tobaccos," were read before the Australasian Assoc. Adv. Science, January, 1900.

A. Liversidge. J. A. Schofield.
F. H. Guthrie. Basil Turner.

William M. Hamlet.

Hemingway, Frank C. R.,
Albyns, Forest Road, Walthamstow.

Works Manager. (1) Matriculated Student of the University of London, with a view to eventually taking his B.Sc. degree. (2) Sometime Analyst with the Illinois Steel Company in Chicago, U.S.A. (3) And since engaged in general research work, particularly on Tin and Arsenic, and Chemistry in connection with Colour making.

D. Lloyd Howard. Thomas Tyrer.
Samuel Hall. B. E. R. Newlands.

Arthur R. Ling.

Henderson, John Brownlie,
Brisbane, Queensland.

Government Analyst for the Colony of Queensland. For about two years Assistant Science Master to Govan School Board, Glasgow, then Student under, and for over a year Research Assistant to, Dr. Dittmar, Anderson's College, Glasgow ("Atomic Weight of Hydrogen," Dittmar and Henderson, 1890, principal work). For about two years Science Master in Brisbane Grammar School, and since June, 1893, Government Analyst to the Colony of Queensland. (Annual Report in Mines Departments of Queensland Reports).

James Robson. Thomas Gray.
Chas. A. Fawsitt. *G. G. Henderson.*

Matthew A. Parker.

Hewitt, Samuel,
3, Chester St., Norwich.

Science Master to Norwich School Board, and Assistant Lecturer and Demonstrator in Chemistry Norwich Technical Institute. Certificated by Board of Education, South Kensington, as qualified to teach Theor. and Pract. Chemistry. One year's experience in Labs. of Technical College, Bradford. Two years as student, Biological Laboratory, Yorkshire College, Leeds.

Francis Sutton. *E. C. Thompson.*
F. Napier Sutton. *James Foulds.*
R. S. Cahill. *T. W. Lockwood.*

Hewitt, William Henry,

115, Fentiman Road, London, S.W.

Science Teacher. (1) Associate in Chemistry of the Royal College of Science. (2) Senior Science Teacher, Strand School, King's College London. (3) (B.A. London University).

William A. Tilden. Chapman Jones.
W. Palmer Wynne. M. O. Forster.
G. T. Morgan.

Hudson, Edmund Foster,

Churcher's College, Petersfield, Hants.

Science Master. B.A. Cambridge, late Scholar and sometime Assistant Demonstrator of Chemistry, St. John's College. 1st Class Natural Sciences Tripos, Part I., 1898. 3rd Class Natural Sciences Tripos, Part II., 1899.

H. Brereton Baker. W. J. Sell.
R. H. Adie. W. T. N. Spivey.
K. C. Browning. H. J. H. Fenton.

Jappé, Adolf,

Broad Oak, Oak Avenue, Bradford.

Analytical Chemist. 3 years pupil, and 7 years and at present Chief Assistant to F. W. Richardson, F.I.C., City Analyst for Bradford, &c. Acknowledged for research assistance by F. W. Richardson in different papers in *J. S. C. I.* Also conjoint author of paper on "Glycerine Estimation" in *J. S. C. I.*, April 30, 1898, and on "Water Softening Power of Soaps," *J. S. C. I.*, 1899, p. 998, &c.

F. W. Richardson. Alfred H. Allen.
H. E. Aykroyd. Walter Leach.
G. W. Slatter.

Jones, Humphrey Owen,

Clare College, Cambridge.

Assistant Demonstrator of the University Chemical Laboratory. B.A. (Camb.). First Class Natural Science Tripos, Parts I and II, with distinction in Chemistry. B.Sc. (London and Wales). Joint author with Mr. H. J. H. Fenton, M.A., F.R.S., of the two papers, "Oxidation of Organic Acids in Presence of Ferrous Iron," and "Oxalacetic Acid."

G. D. Liveing. H. J. H. Fenton.
W. J. Sell. W. T. N. Spivey.
S. Ruhemann.

Kilner, George Washington,

14, St. John's Park, Upper Holloway, N.

Barrister-at-Law. M.A. (London Univ.). Intermediate Science (London Univ.). Student in Chemistry at Northern Polytechnic Institution (Honours Stage).

J. T. Dunn.	Charles E. Cassal.
John Spiller.	*W. H. Corfield.*
Henry Kenwood.	*R. C. T. Evans.*

Lamb, Morris Charles,

Herold's Institute, Drummond Road, Bermondsey, London, S.E.

Head of Leather Dyeing Laboratory, Herold's Institute, London, S.E. Assistant and afterwards Demonstrator for seven years in the Leather Industries Laboratory of the Yorkshire College, assisting Prof. Proctor in Research and Analytical Work. Member (late Sec.) International Association of Leather Trades' Chemists. Contributed a paper (part Research Work) to the Society of Dyers and Colourists on the "Application of Aniline Dyestuffs to Leather." It appeared in the Journal of the Society, July, 1900. Has recently communicated a Research on the Microscopic Detection of the Adulterants of Sumach to the Society of Dyers and Colourists, *Journal of the Society of Dyers and Colourists*, March 1899.

Henry R. Procter.	A. G. Perkin.
Arthur Smithells.	J. J. Hummel.

G. W. Slatter.

Lander, George Druce,

1, Balmoral Road, Nottingham.

Lecturer and Demonstrator in Chemistry, University College, Nottingham. Author of following communications to Transactions of the Chemical Society: *Conjointly with Prof. Japp, F.R.S.*, "Condensation of Benzil with Ethylic Acetoacetate," 1896; "Synthesis of Pentacarbon Rings," Pts. I and II, 1897; "Reduction of Desyleneacetic Acid," 1897. *Conjointly with Prof. Purdie, F.R.S.*, "Optically Active Alkyloxypropionic Acids," 1898; "The Action of Alkyl Iodides on Silver Malate and on Silver Lactate," 1898; and of "Alkylation by means of Dry Silver Oxide and Alkyl Halides," 1900.

T. E. Thorpe.	T. Purdie.
F. R. Japp.	W. Palmer Wynne.

F. Stanley Kipping.

M'Call, William,

Rio Marina, Isola d'Elba, Italy.

Analytical Chemist. Head Chemist and general representative in Italy for Messrs. H. Borner and Co., of London. Four and a half years in the employment of Messrs. Tatlock and Thomson, of Glasgow,

engaged in general analyses. Hold first class certificates of the Glasgow and West of Scotland Technical College in Chemical Engineering and Metallurgy. Three years' experience as chemist and representative in the Mines of Elba for Messrs. H. Borner and Co., Ltd.

R. R. Tatlock. Robt. D. Connell.
R. T. Thomson. James E. Ferguson.
Edmund J. Mills.

Nightingale, Thomas Marginson, B.Sc.,
375, Bridgman Street, Bolton.

Science Teacher. Central Higher Grade Board School, Bolton. Three years Student in the Owens College. B.Sc. (Chemistry and Physics) Victoria University, 1895. Teaching Chemistry for last five years.

H. B. Dixon. W. H. Perkin, jun.
G. H. Bailey. *W. T. Lawrence.*
Wm. A. Bone. *D. L. Chapman.*

Pardy, Alexander,
Pietermaritzburg, Natal, South Africa.

Analyst. Analyst to the Agricultural Department, Natal. I studied Chemistry (Theoretical and Practical) during the years 1894—1897 at the University of Aberdeen, taking both General and Agricultural Chemistry. Hold the Senior Certificate of the Royal Agricultural Society of England, 1897. Received the Diploma in Agriculture of the Aberdeen University, 1897. Am at present in the service of the Natal Government Agricultural Department in charge of the Analytical Department, engaged in the investigation of soil problems, investigating the mealie and maize disease, improvement of soils, selection of fruit, &c., advising farmers; have had numerous papers and reports published on liming, farmyard manure, &c., &c.

F. R. Japp. James Hendrick.
T. S. Murray. Alex. Findlay.
M. S. Stanger Higgs. E. Nevill.

Paul, John,
Bacteriological Institute, Grahamstown, Cape Colony.

Analyst. Chemical Assistant, Colonial Bacteriological Institute, Grahamstown, Cape Colony. Late Chemical Assistant, Pathological Laboratory of the London County Council, Woodford.

Stevenson Macadam. Stevenson Macadam, jr.
W. Ivison Macadam. *J. Falconer King.*
Bernard Dyer. *G. H. Gemmell.*

Pearce, Ernest Vivian,

The Beeches, Hayle, Cornwall.

Chemist to the Mellanear Tin Smelting Co., Hayle. Teacher under the Cornwall County Council, 1896—97. Student at Camborne School of Mines, 1893—95. Chemist to Mellanear Smelting Co. 1895 to present time.

John J. Beringer. John Gill.
William Bate. Henry William Hutchin.
Heinrich Rowland Beringer.

Stapleton, Henry Ernest,

St. John's College, Oxford.

Professor of Chemistry. B.A.; Scholar of St. John's College, Oxford; 1st Class Final Honours School of Chemistry, Oxford, 1899; has worked some time with Dr. Ruhemann, of Caius College, Cambridge, and published with him several papers on Organic Chemistry in the Journal of the Chemical Society; Professor of Chemistry, Presidency College, Calcutta.

V. H. Veley. H. L. Bowman.
Percy Elford. A. Hartridge.
J. E. Marsh.

Thornton, Arthur Lambert,

2, Park Street, Bolton.

Science Teacher under the School Board of Bolton and the Technical Instruction Committee of Bolton. Bachelor of Science (Victoria University). Studied in the Owens College Chemical Laboratories during the years 1891—1894.

G. H. Bailey. H. B. Dixon
W. H. Perkin, jun. *J. F. Thorpe.*
Wm. A. Bone.

Wiechmann, Ferdinand Gerhard, Ph.D.,

771, West End Avenue, New York.

Consulting Chemist. The American Sugar Refining Company, New York. Results of research work published in various American and European journals. Author of "Sugar Analysis," "Lecture Notes in Theoret. Chemistry," "Chemistry: its Evolution and Achievements." Teacher of Chemistry for 14 years at School of Mines, Columbia University. Actively engaged in Sugar-chemistry and technology for 17 years.

Arthur H. Elliott. J. H. Wainwright.
Elwyn Waller. *Marston Taylor Bogert.*
Edmund H. Miller.

Wills, George Sampson Valentine,
"Southwood," Croham Road, South Croydon.
Chemist. Author of "Vegetable Organic Materia Medica." Principal of the Westminster College of Chemistry. Analyst, &c.

A. E. Bell.	*Fred. E. Johnson.*
Lester Reed.	*H. Irving Foster.*
Edward D. Gravill.	*S. Hill.*

Woodbridge, Walter Bourne,
Grey Friars, Chichester.
A. C. G. I. (Chemical Dept.); now engaged in sugar works in N. Germany.

Henry E. Armstrong.	William A. Davis.
Edwin C. Jee.	T. Martin Lowry.

William A. Lethbridge.

Wright, Herbert Edwards,
1, Brewers Street, St. Aldate's, Oxford.
M.A. (Cantab.). Brewer. Student under Professor Graham at Univ. Coll., London. Author of "A Handy-book for Brewers" (Crosby, Lockwood & Son). 1st ed., 1892; 2nd ed., 1897.

Charles Graham.	Alfred Collett Young.
Lawrence Briant.	*A. Boake.*
F. G. Adair Roberts.	*C. H. H. Walker.*

The following Certificates were authorised by Council under Bye-Law I (3):—

Aston, Bernard Cracroft,
Wellington, New Zealand.
Chemist to the N.Z. Agricultural Department. Was for three years Analyst at the Milburn Lime and Cement Works, Dunedin, N.Z.; two years Analyst under Licensing Acts for Province of Otago, N.Z.; for past eighteen months in present position. Joint Author of a paper on the Chemistry of the Poisonous Tutu Plant of N.Z. (*Coriaria, sp.*).

Thomas H. Easterfield. J. M. Mason.

Bilimoria, Hormasji Naoroji, M.A., B.Sc.,
28, Wellington Street, Bombay, India.
Officiating Chemical Examiner to Government, Burma; Officiating Lecturer in Chemistry, Rangoon College, Rangoon. M.A. and B.Sc.

(Bombay), with Honours in Chemistry and Physics. Officiating Chemical Examiner to Government, Burma. Officiating Lecturer in Chemistry, Rangoon College, Rangoon. Past five years' experience in Teaching Chemistry.

Andrew Campbell

Meyer, Hans, Ph.D.,

Prag, Austria, 1 Salmgasse.

Docent and Adjunct of the Imperial and Royal German University. Publications: *Anleitung zur quant. Bestimmung d. organ. Atomgruppen.* Berlin: Jul. Springer, 1897. Auth. translation, "Determination of Radicles in Carbon Compounds," by J. B. Tingle. New York: John Wiley and Sons, 1899. Papers: "Derivatives of picolinic acid and their conversion into α-amidopyridine," **66**, i, 425; "Detection and estimation of alkyl groups attached to nitrogen," **66**, ii, 219. "Estimation &c., II," **68**, ii, 296; "Anemonin" **70**, A., i, 623, "Estimation &c., III," **70**, A., i, 68; "Phthaleins," **70**, A., i, 237, 238; "Phthalein derivatives," **72**, A., i, 69; "Cantharidin," **74**, A., i, 41; "Estimation &c., IV," A., i, 53; "Pilocarpidin," **74**, A., i, 389; "Constitution of phenolphthalein," **76**, i, 707; "Isomerides of Cantharidin," **76**, i, 380; "Anemonin, II," **76**, i, 930; "Action of ammonia on lactones," **76**, i, 9; "Amino-deriv. of cantharidin," [1900]; "Amino-acids," [1900].

Bohuslav Brauner. *William Ramsay.*

Wyndham R. Dunstan.

RAMMELSBERG MEMORIAL LECTURE.

The Rammelsberg Memorial Lecture will be delivered by Professor H. A. Miers, D.Sc., F.R.S., on Thursday, December 13th, 1900, at 8.30, p.m.

RESEARCH FUND.

A meeting of the Research Fund Committee will be held in December. Applications for Grants, to be made on forms which can be obtained on application to the Assistant Secretary, must be received on or before November 30th.

At the next meeting, on Thursday, December 6th, the following papers will be communicated.

"Santalonic acid." By Alfred C. Chapman, F.I.C.

"Ammonium bromide and the atomic weight of nitrogen." By A. Scott.

RICHARD CLAY AND SONS, LIMITED, LONDON AND BUNGAY.

Issued 12/12/1900

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 16. No. 229.

December 6th, 1900. Professor THORPE, C.B., F.R.S., President, in the Chair.

The following certificates were read for the first time:—Messrs. Andrew Charles Aitken, Rio Marina, Isola d'Elba, Italy; Thomas Stewart Barrie, 77, Sinclair Drive, Langside; John Cardew Bedwell, 65, High Street, Colchester; Herbert John Bult, 165, Brixton Hill, S.W.; Gilbert Howard Daniel, 21, Church Walk, Ulverston; Frederick George Donnan, Chemical Laboratory, University College, Gower Street, W.C.; John Alfred Emery, Cinderford, Gloucestershire; Bernard Farmborough Howard, Devon House, Buckhurst Hill, Essex; Nicholas Henry Martin, Ravenswood, Low Fell, Gateshead; Theodore Henry Page, 40, Wilson Road, Camberwell, S.E.; Thomas Slater Price, University College, Sheffield; Lionel Guy Radcliffe, 6, Alma Terrace, Old Trafford, Manchester; William Cecil Ramsden, 13, Effra Road, Rathmines, Dublin; John Talbot, Tunstall House, Harrow; James Waterhouse, Oak Lodge, Court Road, Eltham, Kent; William A. Wayland, 4, Harefield Road, Brockley, S.E.; James Scott Wilson, Bradford Street, Walsall.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—Messrs. Bernard Cracroft Aston; George L. Bennett, M.A.; Hormasji N. Bilimoria, M.A., B.Sc.; Frederick Nisbet Binks; Herbert James Singleton Boyes; Theodore Ridley Burnett, Ph.D.; John Henry Cheeseright; Albert Walter Comber; Alexander Davidson; Arthur Louis William Fechtner; Willie

Ludford Freeman, B.A.; William Gasson; George William Gibbings; John Gibson; Walter Augustus Handcock; William A. Hargreaves, M.A.; George Harker, B.Sc.; Frank C. R. Hemingway; John Brownlie Henderson; Samuel Hewitt; William Henry Hewitt, B.A.; Edmund Foster Hudson, B.A.; Adolf Jappé; Humphrey Owen Jones, B.A., B.Sc.; George Washington Kilner, M.A.; Morris Charles Lamb; George Druce Lander, B.Sc.; William McCall; Hans Meyer, Ph.D.; T. Marginson Nightingale, B.Sc.; Alexander Pardy; John Paul; Ernest Vivian Pearce; Henry Ernest Stapleton, B.A.; Arthur Lambert Thornton, B.Sc.; F. Gerhard Wiechmann, Ph.D.; Walter Bourne Woodbridge; Herbert Edwards Wright, M.A.

Of the following papers, those marked * were read:—

***153. "Santalenic acid." By Alfred C. Chapman, F.I.C.**

The author described the preparation of a crystalline acid by the oxidation of oil of santal wood with a neutral aqueous solution of potassium permanganate. *Santalenic acid* has the formula $C_{18}H_{19}O_2$. It crystallises from dilute alcohol in transparent plates possessing a brilliant pearly lustre, is insoluble in water, but dissolves readily in all the ordinary organic solvents. It melts at 76°, boils without decomposition at 189° (corr.) under a pressure of 28 mm., and distils with steam.

Its rotation has been determined and gives $[\alpha]_D = +18{\cdot}05°$.

Many of its salts have been prepared and analysed. The *methyl ester* is an oily liquid boiling at 232—234° (35 mm.), and has a sp. gr. = 1·0132 at 15°/15°. In a 100 mm. tube at 20° it produces a rotation of −18°13′.

***154. "Ammonium bromide and the atomic weight of nitrogen." By A. Scott.**

During a research having for its chief aim the determination of the hydrogen to oxygen ratio by comparing the equivalents of hydrazine, ammonia, and hydroxylamine, the author found that he could not obtain the same equivalent as Stas for ammonium bromide. The value given by Stas is 98·032, whilst that of the author is 97·996, his highest value being 98·003. This would lower the atomic weight of nitrogen from 14·046 to 14·010, a number much nearer that deduced from the relative densities of oxygen and nitrogen (16.: 14·003).

The bromide used by Stas seems to have contained some impurity, probably platinum, as it turned greyish at 115°, and its greyness increased up to 180°; he was unable to sublime it even in ammonia

without its becoming yellow. The ammonium bromide of the author retains its whiteness at 180° and has been sublimed in ammonia, in a mixture of hydrogen with ammonia and in a vacuum, giving the same results before and after sublimation. The silver bromide had the same composition as that of Stas (57·445 per cent. of silver).

The equivalent for ammonium chloride was also determined, and found to be 53·516, as against 53·532 (Stas) and 53·486 (Marignac).

The silver used was prepared by the reduction of silver nitrate by means of ammonium formate, and was notably better than a sample prepared with the utmost care by the well-known cuprous ammonium sulphite process.

To test the purity of the silver in the severest way, the precipitated silver bromide was reduced by hydrogen, when identical results were obtained with the silver so prepared.

***155. "Relationships of oxalacetic acid." By Henry J. Horstman Fenton, F.R.S., and Humphrey Owen Jones, B.A., B.Sc.**

The authors have continued their investigations on the properties and relationships of free oxalacetic acid, obtained by the oxidation of malic acid in presence of ferrous iron.

The behaviour of the acid towards ammonia, aniline, hydrazine, phenylhydrazine hydroxylamine and urea was discussed as well as the relation of the acid to dihydroxymaleic and dihydroxytartaric acids.

It was also shown that the hydrazone of oxalacetic acid readily loses carbon dioxide when heated with water, yielding the hydrazone of pyruvic acid, but that by a sufficient concentration of hydrogen ions this change is prevented, the hydrazone losing water instead and giving Wislicenus' phenyl-pyrazolone-carboxylic acid; a simple method based upon these changes has been devised for comparing the 'strengths' or 'affinities' of various acids.

***156. "The alkaloids of 'Corydalis cava.' The conversion of corybulbine into corydaline." By James J. Dobbie, D.Sc., M.A., Alex. Lauder, B.Sc., and Photios G. Paliatseas.**

Corydaline, $C_{18}H_{15}N(OCH_3)_4$, differs from corybulbine, $C_{18}H_{16}NO(OCH_3)_3$, by CH_2, and contains four methoxyl groups, whilst the latter alkaloid contains only three (*Trans.*, 1895, **67**, 25). The authors have now proved that corybulbine contains a hydroxyl group and forms a mon-acetyl derivative, $C_{18}H_{15}N(OCH_3)_3O{\cdot}C_2H_3O$. By treatment with concentrated hydrogen iodide the two alkaloids yield the same phenolic derivative, $C_{18}H_{15}N(OH)_4,HI$. Corybulbine can be readily converted into corydaline by treatment with equivalent

quantities of methyl iodide and potassium hydroxide in methyl alcohol solution. The artificial corydaline agrees in melting point, solubility in various reagents and specific rotation with the natural alkaloid. The platinichloride, ethyl sulphate and hydriodide of the natural and artificial substances have been compared and found to be identical.

***157. "The inversion of the optically active *ac*-tetrahydro-β-naphthylamines, prepared by the aid of dextro- and lævo-bromocamphorsulphonic acids." By William Jackson Pope and Alfred William Harvey.**

Dextro-*ac*-tetrahydro-β-naphthylamine dextrobromocamphorsulphonate has been previously prepared from racemic *ac*-tetrahydro-β-naphthylamine hydrochloride (*Proc.*, 1899, **15**, 170); it was now shown that on treating the hydrochloride extracted from the mother liquors with ammonium lævobromocamphorsulphonate, a precipitate of *l-tetrahydronaphthylamine l-bromocamphorsulphonate* falls and may readily be obtained in a pure state. The new salt gives $[\alpha]_D = -86{\cdot}2°$ in solution in absolute alcohol, as against $[\alpha]_D = +86{\cdot}5°$ for its optical antipodes.

It has been shown that in preparing the benzylidene, benzoyl and acetyl derivatives of *d*-tetrahydronaphthylamine the major portion of the base undergoes optical inversion (this vol., 74); on liberating the base from its salts by soda and preparing the hydrochloride considerable racemisation also occurs, the optically active hydrochlorides being only separable with difficulty from the mixed salts; the enantiomorphously-related hydrochlorides gave in aqueous solution $[\alpha]_D = +71{\cdot}9°$ and $-69{\cdot}7°$ respectively. The optical inversion seems to occur during the liberation of the base by soda. *d*-Tetrahydronaphthylamine *d*-camphorsulphonate and its enantiomorphously-related isomeride are more easily purified than the corresponding hydrochlorides; these salts crystallise with half a molecule of water, and, after drying, give in aqueous solution $[\alpha]_D = +47{\cdot}7°$ and $-47{\cdot}4°$. The purest specimen of *d*-tetrahydronaphthylamine, obtained by treating the bromocamphorsulphonate with soda and distilling under reduced pressure, gave $[\alpha]_D = +37{\cdot}24°$ in a 100 mm. tube; this still contained about 30 per cent. of the lævo-rotatory base, so that the pure dextro-base would have given $[\alpha]_D = +96°$ approximately.

Optical inversion attending the liberation of a base from its salts has not been previously observed, but E. Fischer has shown that leucine and glutaminic acid undergo partial racemisation on benzoylation; these substances all contain the group $\begin{matrix}R'\\R''\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}H\\NH_2\end{matrix}$, and the partial optical inversion is probably due to part of the base being moment-

arily converted into a substance containing a group of the type $\frac{R'}{R''}>C:NH_3$ during conversion of an addition compound into one containing triad nitrogen.

***158. "The alkaloids of 'Hyoscyamus muticus' and of 'Datura Stramonium' grown in Egypt." By Wyndham R. Dunstan and Harold Brown."**

In a previous paper (*Trans.*, 1899, **75**, 72), the authors showed that *Hyoscyamus muticus* grown in India contained 0·1 per cent. of hyoscyamine which is readily isolated in a pure state. Subsequently Gadamer (*Archiv der Pharmazie*, 236, **9**, 704) in a brief note recorded the fact that the same plant grown in Egypt contains more than ten times this quantity. Through the kindness of Mr. E. A. Floyer, the authors have been enabled to examine a specimen of the plant from Egypt. They find it to be much richer in hyoscyamine than the sample of Indian growth previously examined. The seeds furnished 0·87 per cent. and the stems and leaves 0·59 per cent. It remains to be determined whether the Indian plant is always poorer in alkaloid or whether it was a peculiarity of the sample examined.

The authors call attention to the Egyptian plant as an important source of the alkaloid hyoscyamine.

Datura Stramonium grown in the Egyptian desert also contains hyoscyamine, unaccompanied by other atropaceous alkaloids, to the extent of 0·35 per cent.

An abundant supply of either plant could be obtained from Egypt.

159. "Interaction of urethanes and primary benzenoid amines." By Augustus Edward Dixon, M.D.

Manuelli and Comanducci have described (*Gazz.*, 1899, **29**, ii, 142) as phenylparatolylcarbamide, PhNH·CO·NHTo, a substance they obtained by heating phenylurethane with paratoluidine; they give its melting point as 259—260°, and confirm the formula by a complete analysis. These chemists have apparently overlooked the descriptions of phenylparatolylcarbamide given by Huhn (*Ber.*, 1886, **19**, 2408), Goldschmidt and Meissler (*Ber.*, 1890, **23**, 273) and the author (*Trans.*, 1895, **67**, 562), who record the melting point as 211°, 211°, and 212—213° respectively; Paal and Vanvolxem (*Ber.*, 1894, **27**, 2426) give its melting point as 212°.

It occurred to the author as just possible that Manuelli and Comanducci's compound might be a 'labile' form of the symmetrical carbamide, for instance, PhN:C(OH)·NHTo; in order to find out if the

discrepancy noted above might be thus explained, the interaction of certain urethanes and aromatic bases was investigated.

Phenylurethane and paratoluidine, when heated together, yielded aniline and a crystalline solid; the latter consisted of a main portion melting at 260—261°, which was proved to be, not phenylparatolyl-, but diparatolyl-carbamide, along with a small quantity of phenylparatolylcarbamide melting at 213—214°. It is suggested that the production of diparatolylcarbamide is due to the expulsion of aniline by toluidine from the phenyltolylcarbamide initially formed, the actions occurring as follows:

(I) $PhNH{\cdot}CO{\cdot}OEt + ToNH_2 = EtOH + PhNH{\cdot}CO{\cdot}NHTo.$

(II) $PhNH{\cdot}CO{\cdot}NHTo + ToNH_2 = PhNH_2 + CO(NHTo)_2.$

Aniline heated with paratolylurethane, gave a solid product which consisted mainly of phenylparatolylcarbamide, m. p. 213—214°, with only a small quantity of a substance melting at about 256—257°, probably diparatolylcarbamide.

From orthotoluidine and phenylurethane, aniline always was liberated, the solid product being a mixture, from which were separated (1) vitreous prisms, melting at 249—250° (diorthotolylcarbamide), and (2) woolly-looking clumps of needles melting at 203—204°; these were nearly pure phenylorthotolylcarbamide. The latter compound, when prepared by acting with silver nitrate on the corresponding thiocarbamide, or from phenyl isocyanate and orthotoluidine, melted at 207—208°.

It seemed, therefore, not improbable that the *s*-phenyl-α-naphthylcarbamide prepared by Manuelli and Comanducci from phenylurethane and α-naphthylamine, and stated to melt at about 277—278°, might prove to be really di-α-naphthylcarbamide; this interaction was therefore re-examined. Phenyl-α-naphthylcarbamide was prepared in two distinct ways and found to melt at 222—223°. Immediately after melting it resolidifies, remelting about 20° higher; the cause of this behaviour has not yet been investigated.

When phenylurethane was heated with α-naphthylamine as described, much aniline was formed, together with a solid mixture, which, when boiled with alcohol, left di-α-naphthylcarbamide, which is nearly insoluble, and melts rather indistinctly at 286—287°; from the extract a small quantity of a substance was deposited which crystallised from alcohol in woolly-looking needles. This melted at about 221°, resolidifying immediately, as described above, and evidently consisted of phenyl-α-naphthylcarbamide.

Manuelli and Comanducci also obtained from normal amylamine and phenylurethane a colourless solid, melting at 238°, which they regard as *ab*-amylphenylcarbamide, but which the author thinks is probably carbanilide.

160. "The decomposition of chlorates. Part III. Calcium chlorate and silver chlorate." By William H. Sodeau, B.Sc.

When calcium chlorate is decomposed slowly, about 0·6 per cent. of its total chlorine is evolved, whether the pressure be 760 mm. or 4 mm., but the proportion exceeds 2 per cent. when the decomposition under atmospheric pressure is rendered violent. As the proportion of free chlorine is independent of the pressure of the gaseous products, the calcium chloride in the residue is not produced by the action of chlorine upon oxide first formed.

When silver chlorate is heated to about 350° it explodes with a yellow flash, about 7 per cent. of its chlorine accompanying the oxygen. When slowly decomposed the influence of pressure is even greater than in the case of lead chlorate (*Trans.*, 1900, **77**, 718). At atmospheric pressure only 0·2 per cent. of its chlorine remains free, but 22·6 per cent. is obtained at 2½ mm. pressure, and more than 36 per cent. should be obtained if the action between chlorine and silver oxide could be completely eliminated.

It is concluded that oxygen and chlorine are produced during the slow decomposition of either chlorate by two simultaneous independent reactions represented by the equations $2M(ClO_3)_2 = 2MCl_2 + 6O_2$ and $2M(ClO_3)_2 = 2MO + 2Cl_2 + 5O_2$ (where M = Ca or Ag_2). With calcium chlorate the "chloride" decomposition proceeds at about 180 times the rate of the "oxide" decomposition, whilst with silver chlorate the ratio is less than 1·8 : 1.

The probability of the "oxide" decomposition being endothermic suggests an explanation of the increase of chlorine in rapid decomposition at high temperature.

Silver chlorate differs from the chlorates of potassium, barium and calcium in its highly explosive nature and in the occurrence of an extremely strong secondary action between chlorine and the oxide, but resembles the chlorates of potassium, barium, calcium and lead, in that no free chlorine is produced by displacement from the chloride.

161. "On iron nitride." By G. J. Fowler, M.Sc.

Nitride of iron was prepared by three different methods: by the action of ammonia on (*a*) finely divided iron, (*b*) ferrous chloride and bromide, (*c*) iron amalgam. Of these methods (*a*) is the most convenient. The substance was found to correspond to the formula Fe_2N. The temperatures of the formation of iron nitride in ammonia and of its decomposition in hydrogen are identical. These results confirm the conclusions of Stahlschmidt. Heated in a current of

nitrogen, iron nitride begins to decompose at about 600°; it is slightly magnetic; its specific gravity is 6·35.

When oxidised in air or oxygen, only traces of oxides of nitrogen are produced; heated in a current of air, the substance begins to be converted into ferric oxide and nitrogen at about 200°. It takes fire in chlorine either spontaneously, or when slightly warmed, ferric chloride and nitrogen being formed, but no trace of nitrogen chloride. It is only slowly attacked by bromine, the action probably being due to the presence of hydrobromic acid in the bromine as an impurity. An ethereal solution of iodine has no action on it.

Dilute hydrochloric and sulphuric acids yield the corresponding ferrous and ammonium salts, hydrogen being liberated, according to the following equation: $2Fe_2N + 6H_2SO_4 = 4FeSO_4 + 2NH_4HSO_4 + H_2$.

The simultaneous action of hydrogen peroxide and sulphuric acid is not distinguishable from that of the acid alone. Nitric acid acts only slowly on the nitride even when strong; the products formed vary with the concentration of the acid.

Gaseous hydrochloric acid begins to attack the nitride at about 220°, and at 350° the reaction becomes rapid, the substance being completely converted into ferrous chloride and ammonium chloride. Gaseous hydrogen sulphide has a precisely similar action at 200°.

Nitric oxide acts similarly to oxygen, and converts the nitride into oxide, the reaction beginning at about 120° and becoming rapid at 170°. Carbon dioxide oxidises the nitride at about 530°. On heating the nitride in steam at 100°, ammonia is very slowly formed. The nitride heated with sodium and carbon yields sodium cyanide.

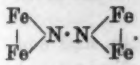
It was thought that phenol might act on nitride of iron in the same way as dilute acids, but the two substances do not react.

On heating with ethyl iodide in a sealed tube to 200—230°, gas is produced consisting chiefly of olefines, with a trace of paraffins, but no amines. The reaction may probably be thus represented: $Fe_2N + 5C_2H_5I = NH_4I + 5C_2H_4 + 2FeI_2$.

162. "The heat of formation and constitution of iron nitride." By Gilbert John Fowler, M.Sc., and Philip J. Hartog, B.Sc.

To determine the heat of formation of iron nitride, the substance was dissolved in dilute sulphuric acid (containing 49 grams to the litre) as represented by the equation $Fe_2N + 3H_2SO_4,Aq = 2FeSO_4,Aq + NH_4HSO_4,Aq + H$. A current of nitrogen was passed through the solution to avoid oxidation of the ferrous salt, as the reaction is a slow one, though it eventually becomes complete. The mean of three determinations gave as the thermal value of the reaction +81·56 cals. From this value the heat of formation of iron nitride is calculated to be

+3·04 cals. It is suggested that the constitution of iron nitride is



163. "Infracampholenic acid: an isomeride of campholytic and isolauronolic acids." By M. O. Forster.

By hydrolysing the unsaturated nitrile formed when the anhydride of bromonitrocamphane is treated with hot, aqueous sodium hydroxide (Trans., 1899, 75, 1141), *infracampholenic acid*, $C_9H_{14}O_2$, is obtained as a viscous oil boiling at 145° and 239°, under pressures of 24 mm. and 758 mm. respectively; it is optically inactive, and is transformed into isolauronolic acid by hot, dilute, sulphuric acid. The *dibromide*, $C_9H_{14}O_2Br_2$, produced when a cold solution of bromine (1 mol.) is added to the acid dissolved in chloroform and surrounded by a freezing mixture, crystallises from warm petroleum in minute, white needles, which melt at 125° to a colourless liquid which evolves gas. *Tribromodihydroinfracampholenic acid*, $C_9H_{12}O_2Br_3$, obtained when infracampholenic acid is submitted to the action of bromine under the conditions which lead to the conversion of campholytic acid into its dibromide, crystallises from ethyl acetate, and melts at 182° to a colourless liquid which evolves gas.

Aminoinfracampholene, $C_8H_{15}\cdot NH_2$, prepared from the amide of infracampholenic acid by the action of sodium hypobromite, is a colourless oil which boils at 158—160° under 754 mm. pressure, and has a sp. gr. 0·8770 at 14°. The *hydrochloride* melts at 213°, the *platinichloride* at 238—240°, and the *picrate* at 213°; the *benzoyl*, *carbamide*, and *phenylcarbamide* derivatives melt at 105°, 182°, and 180° respectively.

164. "Tutu. Part I." By Thomas Hill Easterfield and Bernard Cracroft Aston.

The authors have examined three varieties of tutu—*Coriaria ruscifolia*, *C. thymifolia*, *C. angustissima*—which cause serious loss of stock in New Zealand, and have isolated from them a glucoside, *tutin*, $C_{17}H_{20}O_7$, along with acetic, gallic, succinic and other acids. From *C. thymifolia* quercitin or an isomeric compound was obtained; and from *C. angustissima* a volatile acid, $C_8H_8O_4$, which has not been identified.

Tutin was obtained in colourless crystals melting at 208—209° (uncorr.), and is perceptibly volatile at 120—130°. Its solubility is 1·9 grams in 100 grams water at 10°; 1·5 grams in 100 grams ether at 10°; 8·2 grams in 100 grams alcohol at 16°. It is very soluble in acetone, sparingly soluble in chloroform, insoluble in benzene and

carbon disulphide. Its optical rotation was determined, and gives $[\alpha]_D^{18} = +9{\cdot}25°$.

The authors also discussed the formula for coriamyrtin, and conclude that the formula, $C_{15}H_{18}O_5$, which is half that usually accepted, harmonises better with the facts. A comparison of the chemical and physical characters of tutin and coriamyrtin proved that these substances are not identical.

A note by Professor Marshall on the pharmacology of tutin states that its action is similar to that of coriamyrtin, but is more slowly produced, and it is much less toxic. Its action is exerted mainly on the medulla oblongata and the basal ganglia of the brain.

165. "Experiments on the production of optically active compounds from inactive substances. Preliminary notice." By J. B. Cohen and C. E. Whiteley.

E. Fischer has shown (*Annalen*, 1892, **270**, 64) that in the synthesis of one sugar from another by the addition of hydrocyanic acid to the lower member, a new asymmetric carbon atom is introduced, which may give rise to two stereoisomeric compounds. This may be represented as follows:

$$-C\lessdot^{O}_{H} + HCN = -\overset{H}{\underset{CN}{C}}-OH \quad \text{and} \quad HO-\overset{H}{\underset{CN}{C}}-$$

Although the two new groups are optical antipodes, the two isomerides are not necessarily so as a whole, and consequently they are not always produced in equal quantities. Fischer has found, for example, that glucose forms two cyanhydrins in very unequal quantities, whilst in the case of dextro-mannose only one of the two possible cyanhydrins is produced (Hartmann, *Annalen*, 1892, **272**, 190). It is clear, therefore, that the asymmetric molecule as a whole exerts its influence on the space configuration of the newly added asymmetric carbon group. In these examples, it is impossible to determine exactly the influence of the active part of the original molecule on the activity of the new group, seeing that the latter cannot be detached from the molecule. As the formation of active substances in living organisms is probably closely connected with their production from other active substances from which they are afterwards removed, the idea occurred to us to attempt to produce a new asymmetric carbon atom in an already active compound from which the originally active group could be subsequently detached.

A number of reactions readily presented themselves, such as the

reduction, bromination or hydroxylation of esters composed of an unsaturated acid and an active alcohol, or the reduction of a ketonic ester of an active alcohol, the alcohol being afterwards removed by hydrolysis.

These reactions may be represented as follows: (X stands for an atom or group not being hydrogen, A indicates the active alkyl or aryl group, and C, the new asymmetric carbon atom):

1. (*a*) $\cdot CH{:}CX\cdot CO_2A$ (*b*) $\cdot CH_2\cdot CHX\cdot CO_2A$ (*c*) $\cdot CH_2\cdot CHX\cdot CO_2H$.
2. (*a*) $\cdot CH{:}CH\cdot CO_2A$ (*b*) $\cdot CHX\cdot CHX\cdot CO_2A$ (*c*) $\cdot CHX\cdot CHX\cdot CO_2H$.
3. (*a*) $\cdot CO\cdot CO_2A$ (*b*) $\cdot CHOH\cdot CO_2A$ (*c*) $\cdot CHOH\cdot CO_2H$.

Under (1) we have studied the reduction of the menthyl esters of mesaconic and phenylcrotonic acids.

(*a*) $CH_3\cdot C(CO_2C_{10}H_{19}){:}CH\cdot CO_2C_{10}H_{19}$

(*b*) $CH_3\cdot CH(CO_2C_{10}H_{19})\cdot CH_2\cdot CO_2C_{10}H_{19}$ (*c*) $CH_3\cdot CH(CO_2H)CH_2\cdot CO_2H$.

(*a*) $C_6H_5\cdot CH{:}C(CH_3)\cdot CO_2C_{10}H_{19}$

(*b*) $C_6H_5CH_2\cdot CH(CH_3)\cdot CO_2C_{10}H_{19}$ (*c*) $C_6H_5CH_2\cdot CH(CH_3)\cdot CO_2H$.

Under (2) we have prepared the bromine derivatives of the amyl and menthyl esters of cinnamic acid and of dicinnamyl tartrate, and examined the action of various reagents on the dibromo-compounds, also the action of sodium ethylate on menthyl fumarate.

(*a*) $C_6H_5CH{:}CH\cdot CO_2C_5H_{11}$ (*b*) $C_6H_5CHBr\cdot CHBr\cdot CO_2C_5H_{11}$.

(*a*) $C_6H_5CH{:}CH\cdot CO_2C_{10}H_{19}$ (*b*) $C_6H_5CHBr\cdot CHBr\cdot CO_2C_{10}H_{19}$.

(*a*) $\begin{matrix} C_6H_5CH{:}CH\cdot CO_2\cdot CH\cdot CO \\ C_6H_5CH{:}CH\cdot CO_2\cdot CH\cdot CO \end{matrix}\!\!>\!O$ (*b*) $\begin{matrix} C_6H_5CHBr\cdot CHBr\cdot CH\cdot CO_2H \\ C_6H_5CHBr\cdot CHBr\cdot CH\cdot CO_2H \end{matrix}$.

(*a*) $\begin{matrix} CH\cdot CO_2\cdot C_{10}H_{19} \\ \| \\ CH\cdot CO_2\cdot C_{10}H_{19} \end{matrix}$.

Under (3) we have investigated the reduction of menthyl pyruvate.

(*a*) $Me\cdot CO\cdot CO_2C_{10}H_{19}$ (*b*) $Me\cdot CHOH\cdot CO_2C_{10}H_{19}$ (*c*) $Me\cdot CHOH\cdot CO_2H$.

The results in all cases have been of a negative character, in spite of every care to avoid possible racemisation by conducting the reactions as far as possible at the ordinary temperature.

The experiments, which were commenced in 1898, have been delayed in consequence of unforeseen difficulties. All the experiments under (2), after a considerable loss of time, had to be abandoned. Although the dibromo-derivatives of amyl and menthyl cinnamate and of dicinnamyl tartrate could be readily obtained in a state of purity, they could not be directly hydrolysed without removing bromine, and all attempts to replace the bromine by hydroxyl failed. Menthyl fumarate, which was readily prepared from silver fumarate and menthyl chloride, gave

no ethoxy-derivative by means of Purdie's reaction. Reactions (1) and (3) were, however, ultimately brought to a satisfactory conclusion.

Menthyl mesconate and menthyl phenylcrotonate were prepared by heating together menthol and the acid chloride, whilst menthyl pyruvate was obtained by heating menthol and pyruvic acid under diminished pressure. The reduction of the first two esters was effected by means of the aluminium-mercury couple in aqueous alcoholic solution, whilst menthyl pyruvate was reduced with zinc dust and acetic acid. The esters were then hydrolysed with alcoholic potash and the menthol removed with ether. The acid, after careful purification by crystallisation or precipitation of its salt, was finally examined in the polarimeter. Pyrotartaric acid, phenylmethylacetic acid, and lactic acid, obtained in this way, were all optically inactive. We propose to extend these experiments to the acid amides of optically active bases.

166. "Synthesis of isocamphoronic acid." By W. H. Perkin, jun.

When the anhydride of $CO_2H\cdot CMe_2\cdot CH_2\cdot CH_2\cdot CO_2H$, *aa*-dimethylglutaric acid, is treated with phosphorus pentachloride and bromine and the product poured into alcohol, $CO_2Et\cdot CMe_2\cdot CH_2\cdot CHBr\cdot CO_2Et$, *ethyl bromodimethylglutarate* is obtained as a colourless oil boiling at 165—170° (35 mm.).

This on treament with alcoholic potash yields *dimethylglutaconic acid*, $CO_2H\cdot CMe_2\cdot CH{:}CH\cdot CO_2H$, which crystallises from water in plates melting at 172° and is possibly a stereoisomeride of the *aa*-dimethylglutaconic acid lately prepared by M. Conrad (*Ber.*, 1900, **33**, 1920) which melts at 150°. That the acid of melting point 172° has the constitution assigned to it is proved by the fact that when oxidised with permanganate at 0° it is quantitatively converted into dimethylmalonic acid and oxalic acid,

$$CO_2H\cdot CMe_2\cdot CH{:}CH\cdot CO_2H + 3O = CO_2H\cdot CMe_2\cdot CO_2H + CO_2H\cdot CO_2H.$$

Dimethylglutaconic acid is readily esterified by means of alcohol and sulphuric acid: the *ethyl dimethylglutaconate*, $CO_2Et\cdot CMe_2\cdot CH{:}CH\cdot CO_2Et$, thus produced, is a colourless oil boiling at 200° (200 mm.).

When this ester is digested in alcoholic solution with the sodium compound of cyanacetic ester, condensation takes place, and the product, on heating with dilute sulphuric acid, is almost quantitatively converted into an acid melting at 166°, and which on examination has been proved to be *isocamphoronic acid*.

(Found C = 49·7; H = 6·5; $C_9H_{14}O_6$ requires C = 49·5; H = 6·4.)

Professor von Baeyer was kind enough to send the author a sample of isocamphoronic acid which had been prepared from pinene, and on mixing equal quantities of this and the synthetical acid, no altera-

tion in the melting point could be observed. Again, when heated with sulphuric acid at 100°, the synthetical acid is converted into *terpenylic acid*, a change which Tiemann (*Ber.*, 1896, **29**, 2613) has shown to be characteristic of isocamphoronic acid.

There can thus be no doubt that the synthetical acid is in reality isocamphoronic acid, and its synthesis solves the vexed question of the constitution of this important acid.

The condensation of ethyl dimethylglutaconate with the sodium compound of ethyl cyanacetate may be represented thus:

$$CO_2Et\cdot CMe_2\cdot CH{:}CH\cdot CO_2Et + CN\cdot CHNa\cdot CO_2Et = CO_2Et\cdot CMe_2\cdot \underset{CN\cdot CH\cdot CO_2Et}{CH}\cdot CHNa\cdot CO_2Et,$$

and the cyanester thus produced yields, on hydrolysis and elimination of carbon dioxide, isocamphoronic acid, which, therefore, must have the constitution, $CO_2H\cdot CMe_2\cdot CH(CH_2\cdot CO_2H)\cdot CH_2\cdot CO_2H$, first proposed for this acid by Tiemann (*Ber.*, 1896, **29**, 2614).

167. "On some α-alkyl substitution products of glutaric, adipic, and pimelic acids." By J. W. Mellor.

The author describes the known methods of general application for the preparation of the above acids, and gives an account of some new methods which he has employed in synthesising such acids. He finds that adipic acid itself may be readily prepared in quantity by the action of *chloropropylcyanide*, $Cl\cdot CH_2\cdot CH_2\cdot CH_2\cdot CN$, on the sodium compound of ethyl malonate, and subsequent hydrolysis of the *ethyl cyanpropylmalonate*, $CN\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(CO_2Et)_2$ (b. p. 170—175° at 40 mm.), by boiling with dilute sulphuric acid. α-Alkyl substitution products of adipic acid may be obtained by employing the corresponding ethyl α-alkylmalonates in this synthesis in the place of ethyl malonate.

The author has prepared several of the known α-alkyl substitution products of glutaric, adipic, and pimelic acids in a state of purity, and determined their dissociation constants. He has also prepared *α-propyl adipic acid*, $CO_2H\cdot CHPr\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO_2H$, which melts at 59° and does not appear to have been previously described.

168. "On the nature of polyiodides and their dissociation in aqueous solutions." By H. M. Dawson.

From experiments on the ratio of distribution of iodine between solutions of potassium iodide and carbon bisulphide and the simplicity of the dissociation isotherm for the equilibrium in the aqueous solution, which accords with the experimental data, it is concluded that

potassium triiodide is a normal salt of potassium, which at corresponding concentrations is dissociated electrolytically to the same extent as other binary salts. Experiments with solutions of hydriodic acid lead to the conclusion that hydrogen triiodide is electrolytically dissociated to the same extent as hydriodic acid, and belongs, therefore, to the group of strong acids. These results are in harmony with Abegg and Bodländer's theory of complex compounds. From their analogy with potassium triiodide, the recently discovered trihaloid derivatives of cæsium and rubidium must be placed in the same category.

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RAMMELSBERG MEMORIAL LECTURE.

The Rammelsberg Memorial Lecture will be delivered by Professor H. A. Miers, D.Sc., F.R.S., on Thursday, December 13th, 1900, at 8.30 p.m.

At the next meeting, on Thursday, December 20th, the following paper will be communicated.

"On the union of hydrogen and chlorine." By J. W. Mellor, B.Sc.

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Issued 9/1/1901

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 16. **No. 230.**

December 13th, 1900. Extra Meeting. Professor THORPE, C.B., F.R.S., President, in the Chair.

Professor H. A. MIERS, D.Sc., F.R.S., delivered the Rammelsberg Memorial Lecture.

Karl Friedrich Rammelsberg was born on April 1st, 1813, at Berlin, and succeeded Heinrich Rose as Professor of Inorganic Chemistry in the University of Berlin in 1874. He was also Instructor in Chemistry (1850—1883) at the Gewerbe-akademie, which became the Technische Hochschule and was transferred to Charlottenburg in 1883; from 1883 to 1891, he was Director of the Second Chemical Institute of the University. He was twice married; in 1846, to the daughter of Oberbergrath Zincken; in 1859, to the daughter of C. G. Ehrenberg. In 1841, as Privatdocent, he started a private laboratory, in which was given the first practical chemical instruction in Berlin. He published an immense number of papers dealing with inorganic chemistry, crystallography, and mineralogy, but never himself engaged in any research work relating to organic chemistry. He was the author of numerous chemical text-books, one of which, *Grundriss der Chemie gemäss den neueren Ansichten* (1866), was the first to explain the new principles of organic chemistry. He was also the first of the old school of chemists to adopt the new system of formulæ.

Two of his books were encyclopædic works of reference: the *Handbuch der Krystallographischphysikalischen Chemie* (1855—1881) contained the crystallographic, optical, and physical constants of all crystallised compounds; the *Handbuch der Mineralchemie* (1841—1895) was an exhaustive treatise on the composition of all minerals.

He was equally eminent as Inorganic Chemist, Crystallographer, and Mineralogist. In chemistry, his work upon the halogen compounds, the phosphates, and the cyanides may be taken as samples of his researches. He prepared and studied an enormous number of bromides, of the ammonia compounds of the bromides and iodides; of bromates, iodates, and periodates; of phosphates, phosphites, and hypophosphites; our knowledge of the double cyanides is almost entirely due to him; equally laborious and important were his researches upon the sulphantimonates, hyposulphites, sulphites, nitrites, vanadates, phosphomolybdates. One of his important papers, on the Mexican amalgamation process, was communicated to this Society (1881). In crystallography, he did more than any other man to carry on the work of Mitscherlich, and investigated an immense number of isomorphous compounds; he studied the isomorphism of sulphur and selenium; he pointed out the isomorphism of vanadinite and pyromorphite, and first suggested that vanadic acid is V_2O_5; in his work upon the crystallisation of the sulphates $RSO_4,7H_2O$ from mixed solutions, he was one of the pioneers of modern physical chemistry.

In mineralogy also he contributed more than any one to our knowledge of the composition of minerals and was practically the father of modern mineral chemistry; he published more than 300 papers on mineralogical subjects (including those on the analysis of rocks and meteorites); he first established the presence and the relationship of the ferrous and ferric iron in the group of the augites and hornblendes; he was the first to accept Tschermak's theory of the felspar group; and his laborious analyses ranged over about two-thirds of the mineral kingdom; he was strongly opposed to Penfield's views on the mutual replacement of fluorine and hydroxyl. Rammelsberg's active labours in mineral chemistry continued to the end of his long life, and at the age of 82 he published an elaborate supplement to his *Handbuch der Mineralchemie*. He died on December 28th, 1899, at Gross Lichterfelde, near Berlin, after a life of almost unexampled industry.

On the motion of Dr. Hugo Müller, seconded by Professor M'Leod, a vote of thanks was passed to Professor Miers for his Lecture.

December 20th, 1900. Professor Thorpe, C.B., F.R.S., President, in the Chair.

The following certificates were read for the first time: Messrs. Merrick William Burrows, Dunkirk, Devizes; Robert Waley Cohen, 11, Hyde Park Terrace, London, W.; Reginald Williams Ferguson,

8, Havelock Terrace, Paisley Road, Glasgow; John Lloyd Thomas Jones, United Service Club, Calcutta; James Menzies, 39, Winterbrook Road, Herne Hill, London, S.E.; Arthur W. Nunn, 313, Sydenham Road, Sydenham, S.E.; Herbert Kilburn Scott, P.O. Box 634, Rio de Janeiro, Brazil; Albert Edward Thomas, 34 South Road, Kingswood, Bristol.

Of the following papers, those marked * were read :—

***169. "On the union of hydrogen and chlorine." By J. W. Mellor, B.Sc.**

At the suggestion of Professor H. B. Dixon the author undertook to investigate the mode in which light brings about the combination of hydrogen with chlorine. The electrolysis of hydrochloric acid and of the solution of chlorine in this acid were first studied, as an exact knowledge of these is necessary to interpret the work of previous investigators.

Bunsen and Roscoe state that under certain conditions the gas resulting from the electrolysis of hydrochloric acid consists of a practically pure mixture of hydrogen and chlorine. The author finds, however, that under the most favourable conditions oxygen is present to the extent of 0·009 per cent.

In order to find out if the distribution of the gases in Bunsen and Roscoe's insolation vessel is affected by the absorption of hydrogen chloride, a more complete investigation was made. By plotting the respective amounts of chlorine and hydrogen chloride in the solution, it is found that two distinct and intersecting curves appear: (1) If the hydrochloric acid be less than one-fifth of normal strength, the amount of chlorine absorbed decreases as the amount of hydrogen chloride increases. The explanation is based on Jakowkin's work on the distribution ratio of chlorine between water and carbon tetrachloride where the action of chlorine on water (in darkness) is shown to be a trimolecular one

$$Cl_2Aq \rightleftharpoons (\overset{+}{H} + \overset{-}{Cl} + HOCl)Aq.$$

The number of $\overset{+}{H}$ and $\overset{-}{Cl}$ ions is evidently increased by the addition of hydrogen chloride, and therefore, in agreement with Nernst's distribution law, the number of ions derived from the chlorine is diminished. This involves a decrease in the solubility of that gas.

(2) If the strength of the solutions of hydrochloric acid be greater than one-fifth of the normal the amount of chlorine (λ) absorbed *increases* as the amount of hydrogen chloride (p) increases.

The increase is a linear function of the amount of hydrogen chloride present. $\lambda = 0{\cdot}07p + 1{\cdot}528$.

The phenomenon is probably due to the formation of a compound of hydrogen chloride with the chlorine, say HCl_3. There is no sharply defined point of transition, because the phases $\overset{+}{H} + \overset{-}{Cl} + HCl_3$, &c., co-exist in the solution.

A slight contraction occurs when chlorine and hydrogen chloride gases are allowed to diffuse into each other.

***170. "The nitration of the three tolueneazophenols." By J. T. Hewitt and J. H. Lindfield.**

The three tolueneazophenols have been nitrated by warm dilute nitric acid, and in each case the nitro-group has been found to enter the phenol nucleus in the ortho-position relatively to the hydroxyl. This agrees with the results previously obtained in the cases of oxyazobenzene and benzeneazosalicylic acid.

The following substances were described: o-*Tolueneazo-o-nitrophenol*, m. p. 146°; the *ethyl ether*, m. p. 93°; the *acetate*, m. p. 120·5°; the *benzoate*, m. p. 132°.

m-*Tolueneazo-o-nitrophenol*, m. p. 128·5°; the *ethyl ether*, m. p. 92°.

p-*Tolueneazo-o-nitrophenol*, m. p. 147°; the *ethyl ether*, m. p. 116°; the *acetate*, m. p. 94°; the *benzoate*, m. p. 129°.

The conditions under which *m*-tolueneazo-*o*-nitrophenol can be acetylated or benzoylated have not been discovered, as excess of benzoyl chloride fails to change the substance. The other acylations take place easily and normally. It is also noteworthy that difficulty is experienced in alkylating *o*-tolueneazo-*o*-nitrophenol with sodium ethoxide and ethyl bromide; the other alkylations are, however, normal.

The *ethyl ether* of *benzeneazo-o-nitrophenol* was prepared for purposes of comparison; it melts at 93°.

Discussion.

Dr. George Young inquired what evidence there was to show that acetylisation of a hydroxyazo-compound always produced an acetoxy- and not an acethydrazone derivative. It seemed curious that a change of position of a methyl group in the benzene should influence the acetylisation of the phenol side of the molecule.

Dr. Hewitt, stated that though Goldschmidt claimed to have com-

pletely reduced the acetyl derivative of benzeneazo-*p*-cresol to acetanilide and *p*-cresol, MacPherson had obtained compounds by the action of benzoylphenylhydrazine on quinones which were isomeric and not identical with the benzoyl derivatives of the azophenols. Hence it would appear that the acetyl and benzoyl derivatives of the azophenols are true oxygen ethers.

***171. "The bromination of the ortho-oxyazo-compounds and its bearing on their constitution." By J. T. Hewitt and H. A. Phillips.**

The effect of substituting agents on numerous oxyazo-compounds of the *para*-series has been studied by one of the authors of this communication and his pupils. So far, bromination or nitration of *ortho*-oxyazo-compounds has not been examined, but it was expected that such compounds would behave as *ortho*quinone-hydrazones, and substitute in the nucleus which had been derived from the diazotised aromatic base. Thus benzeneazo-*p*-cresol was expected to give *para*- or *ortho*-bromobenzeneazo-*p*-cresol, whereas experiment has shown that when the substance is dissolved in glacial acetic acid with an excess of sodium acetate and then brominated, benzeneazo-*o*-bromo-*p*-cresol results. Ortho-oxyazo-compounds appear thus to react towards bromine as true oxyazo-compounds.

In the course of this investigation, the following compounds have been prepared and their properties examined :

Benzeneazo-o-bromo-p-*cresol*, m. p. 123°; *benzeneazo-o-bromo*-p-*cresyl acetate*, m. p. 83°; *benzeneazo-o-bromo*-p-*cresyl benzoate*, m. p. 110°; *o-bromobenzeneazo*-p-*cresol*, m. p. 116°; *o-bromobenzeneazo*-p-*cresyl acetate*, m. p. 85; *o-bromobenzeneazo*-p-*cresyl benzoate*, m. p. 106·5°; *m-bromobenzeneazo*-p-*cresol*, m. p. 112°; *m-bromobenzeneazo*-p-*cresyl acetate*, m. p. 61—62°; *m-bromobenzeneazo*-p-*cresyl benzoate*, m. p. 94°; *p-bromobenzeneazo*-p-*cresol*, m. p. 147°; *p-bromobenzeneazo*-p-*cresyl acetate*, m. p. 123°; *p-bromobenzeneazo*-p-*cresyl benzoate*, m. p. 112°.

172. "On the use of pyridine for molecular weight determinations by the ebullioscopic method." By William Ross Innes.

The author described the precautions necessary to obtain accurate results. The constant for pyridine is 29·5.

Acids, alcohols, and phenols were shown to give normal molecular weights. Pyridine, therefore, does not favour the association of dissolved substances.

173. "The influence of the methyl group on ring formation." By A. W. Gilbody and C. H. G. Sprankling.

The authors have prepared and analysed *p*-ethoxyphenylsuccinamic acid and the following alkyl substituted derivatives. (1) *p-ethoxyphenylsuccinamic acid*, m. p. 166—167°; (2) *methyl-p-ethoxyphenylsuccinamic acid*, m. p. 149—150°; (3) as-*dimethyl* p-*ethoxyphenylsuccinamic acid*, m. p. 160—161°; (4) trans-s-*dimethyl*-p-*ethoxyphenylsuccinamic acid*, m. p. 184—185°; (5) cis-s-*dimethyl*-p-*ethoxyphenylsuccinamic acid*, m. p. 155—156°; (6) *trimethyl-p-ethoxyphenylsuccinamic acid*, m. p. 128—129°; (7) iso*propyl*-p-*ethoxyphenylsuccinamic acid*, m. p. 151—152°.

Two forms of the asymmetrically substituted acids should exist according to theory, but only one has been observed during the research. The anilides of the corresponding phenylsuccinamic acids also seem to behave in a similar manner, for previous investigators have found only one acid, where two might be expected.

The scanty evidence at our disposal (Blaise, *Compt. rend.*, 1898, 126, 753) tends to show that of the two formulæ for methyl-*p*-ethoxyphenylsuccinamic acid, for example,

$$\begin{matrix} CH_3\cdot CH\cdot CO_2H \\ | \\ CH_2\cdot CO\cdot NH\cdot C_6H_4OC_2H_5 \end{matrix} \quad \text{and} \quad \begin{matrix} CH_2\cdot CO_2H \\ | \\ CH_3\cdot CH\cdot CO\cdot NH\cdot C_6H_4OC_2H_5, \end{matrix}$$

the former is the correct one.

Under the conditions employed, the lower members of the series readily yielded anhydrous sodium salts, but the salts of the trimethyl- and isopropyl- "aminic" acids have not so far been obtained pure, owing to the easy formation of the ring compounds (pyrantins).

The above acids were then converted into the corresponding *p*-ethoxyphenylsuccinimide (pyrantin) derivative and the stability of the substituted succinimide ring so produced estimated according to the well-known equation, $\frac{I}{T}\frac{X}{A-x} = Ac$; the figures given being the mean of two or more determinations (compare Miolati and Longo, *Att. Accad. Lincei Rend.*, 1894, [v], 3, 515, 597; 1895, [v], 4, 351; Miolati and Lotti, 1896, [v], 6, 88; Piutti, *Ber.*, 1896, 29, 85).

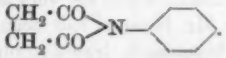
It was necessary to carry out the experiments in alcoholic solution because of the insolubility of the substances in water.

Pyrantin m. p. 155°	Ac = 0·0949	*cis-s*-Dimethyl-pyrantin m. p. 114—115°	Ac = 0·1393
Methylpyrantin .....m. p. 105—106°	Ac = 0·1831	Trimethyl-pyrantin. m. p. 87—88°	Ac = 0 0446
as-Dimethyl-pyrantin m. p. 70—71°	Ac = 0·0872	*iso*Propyl-pyrantin. m. p. 98—99°	Ac = 0·1432

The stability constant was determined for phenylsuccinimide in both aqueous and alcoholic solution, in order to compare the results obtained with those of Miolati for the tolyl- and xylyl-succinimides in aqueous solution.

Phenylsuccinimide was found to be 40·03 times more stable in alcoholic than in aqueous solution, and a correction had also to be made for the value of the ethoxyl group which decreased the stability in alcoholic solution 1·704 times.

The results can then be calculated and tabulated, for the methyl substituted phenylsuccinimides.



	Ac found. Pyrantin in alcoholic solution.	Ac calculated. Phenylsuccinimide in alcoholic solution divided by 1·704.	Ac calculated. Phenylsuccinimide in aqueous solution (G. and S.) multiplied by 40·03; or found (Miolati).
Pyrantin	0·0949	0·0557	2·23
Methylpyrantin.....	0·1831	0·1075	4·30
Isopropylpyrantin	0·1432	0·0840	3·36
cis-Dimethylpyrantin ...	0·1393	0·0818	3·27
Phenylsuccinimide..... ..	Mean of both Miolati	& authors' experi	ments. 2·23
as-Dimethylpyrantin.....	0·0872	0·0512	2·05
3 : 5-Xylylsuccinimide ...	—	—	1·145
p-Tolylsuccinimide.....	—	—	1·12
m- ,, ...	—	—	1·10
Trimethylpyrantin.....	0 0446	0·0262	1·05
2 : 5-Xylylsuccinimide ...	—	—	0·88
o-Tolylsuccinimide.....	—	—	0·856
2 : 3-Xylylsuccinimide ...	—	—	0·815
2 : 6- ,, ...	—	—	0·16

A glance at the above table easily shows in how great a degree the stability of the succinimide ring can be decreased by the introduction of methyl groups into the fatty ring, whereas Miolati's experiments prove that the introduction of methyl groups into the aromatic nucleus increase the stability.

Substances having the constitution formulated above but containing methyl groups in both rings do not appear to have been prepared, although the list given is long enough to anticipate the result which might be expected in such cases.

The reason the authors chose the pyrantins and calculated the

results was that they might obtain some information about the antipyretic action of the methyl group, but unfortunately the substances obtained proved so insoluble in water that no definite result has been obtained.

174. "Experiments on the production of optically active compounds from inactive substances." By F. Stanley Kipping, Ph.D., D.Sc., F.R.S.

The note by Cohen and Whiteley under the above title (this vol., p. 212) deals with experiments which are very similar to some in which the author, assisted by Mr. Hunter, has been recently engaged, the results of which it thus becomes desirable to place on record.

Guided by practically the same considerations, and working with the same object as Cohen and Whiteley, attempts have been made to prepare directly unequal quantities of two enantiomorphously related substances by synthesising an asymmetric carbon group in presence of, or in combination with, some optically active compound, in the hope that the latter would have some directive action on the atoms or groups entering into combination.

Among those experiments in which an optically active substance was used merely as a medium in which the synthesis took place, mention may be made of the preparation of benzoin by the action of potassium cyanide on benzaldehyde in a concentrated alcoholic solution of camphor; mandelic nitrile was also prepared from benzaldehyde and hydrogen cyanide in an alcoholic solution of camphor and then hydrolysed with hydrochloric acid; pyruvic acid and methyl ethyl ketone were also separately reduced in concentrated glucose solution. The results were negative in all these cases.

Among the experiments in which the optically active substance was combined with the inactive nucleus the following may be noted. The reduction of quinine pyruvate and of quinine lævulinate with sodium amalgam or aluminium amalgam; the reduction of *bornyl pyruvate* (b. p. 149—150°, 15 mm.); the reduction of the *oxime* (m. p. about 90°) of bornyl pyruvate, and the reduction of bornyl lævulinate (b. p. 170—171°, 20—25 mm.). After eliminating the original optically active base or alcohol, the product, namely, lactic acid, α-amidopropionic acid, or γ-hydroxyvaleric acid (as lactone), as the case might be, was found to be inactive.

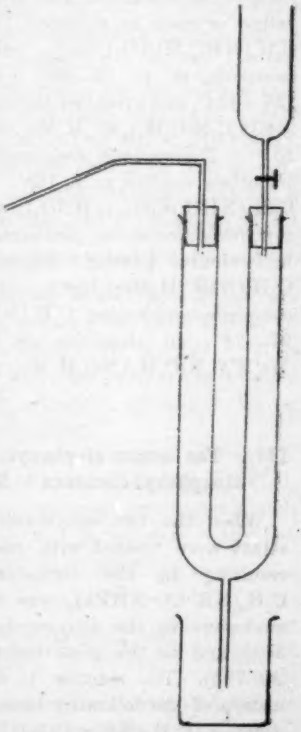
Owing to its low specific rotation and the difficulty of isolating it, the experiments in which lactic acid was obtained are by no means satisfactory, and mandelic acid, which has a high specific rotation, was therefore prepared by the reduction of *bornyl benzoylformate*; this ethereal salt separates from light petroleum in crystals melting at

about 78°, and is reduced to the corresponding hydroxy-salt by sodium amalgam in presence of a little acetic acid; after hydrolysis with potash, it gave inactive mandelic acid.

The failure of these experiments may be caused by racemisation taking place during hydrolysis of the original product, and this possibility is being investigated; even the apparently strong evidence obtained by combining these results with those of Cohen and Whiteley can hardly be considered to settle the question as to the possibility of directly synthesising *unequal* quantities of enantiomorphously related forms, in view of the actual results obtained in the case of the sugars and the theoretical conclusions by which they may be supported.

175. "A lecture table experiment for the preparation of nitric oxide." By Alfred Senier.

When nitric oxide is prepared by the interaction of copper and diluted nitric acid in a flask in the ordinary way, a difficulty arises owing to the accumulation of water. This gives rise to the formation of a large proportion of nitrous oxide. By employing concentrated nitric acid and an excess of copper in the apparatus shown this may be obviated. The figure explains itself. In the apparatus employed the U-tube has a diameter of 3 cm., and together with the small tube beneath measures 36 cm. in height. The larger tube is loosely packed with copper turnings, water is put into the beaker below, and nitric acid (68 per cent.) is dropped from the stoppered funnel. Each drop of acid acts on the copper, liberating nitric oxide, while a solution of cupric nitrate and dilute nitric acid passes into the beaker. The gas after ascending the second arm of the U-tube is quite colourless, and contains only traces of nitrous oxide as shown by absorption with ferrous sulphate.



176. "The action of ethylene dibromide on xylidine and pseudocumidine." By Alfred Senier and William Goodwin.

The reaction between ethylene dibromide and aniline originally studied by Hofmann, and extended to homologues of both compounds by subsequent observers, has been applied to xylidine and pseudocumidine. Dixylylethylenediamine and dicumylethylenediamine were obtained, together with their related piperazines. From the diamines, derivatives were prepared homologous with those obtained by Mills (*Trans.*, 1900, **77**, 1020). *Dixylylethylenediamine*, $C_2H_4(NHC_6H_3Me_2)_2$, white, feathery crystals, m. p. 74—75°. *Dixylylethylenediamine nitrate*, $C_2H_4(NHC_6H_3Me_2)_2(HNO_3)_2$, m. p. 166°. *Dixylylethylenediamine platinichloride*, $C_2H_4(NHC_6H_3Me_2)_2(HCl)_2,PtCl_4$, bright yellow crystals. *Dixylylethylenediamine mercurichloride*, $C_2H_4(NHC_6H_3Me_2)_2HgCl_2$, pale yellow crystals, m. p. about 118°. *Tetranitrodixylylethylenediamine*, $C_2H_4[NHC_6H(NO_2)_2Me_2]_2$, pale yellow crystals, m. p. 220°. An *isomeride*, m. p. 52—53°. *Mononitrodixylylethylenediamine*, m. p. 152—154°, and a *trinitro*-derivative, m.p. 191—192°. *Dixylylpiperazine*, $Me_2H_3C_6N(C_2H_4)_2NC_6H_3Me_2$, consists of shining, white leaflets, m. p. 151°. *Dipseudocumylethylenediamine*, $C_2H_4(NHC_6H_2Me_3)_2$, brilliant, colourless needles, m. p. 168°. *Dipseudocumylethylenediamine nitrate*, $C_2H_4(NHC_6H_2Me_3)_2(HNO_3)_2$, colourless needles, m. p. 154°. *Dipseudocumylethylenediamine platinichloride*, $C_2H_4(NHC_6H_2Me_3)_2(HCl)_2PtCl_4$, buff-coloured powder. *Dipseudocumylethylenediamine mercurichloride* $C_2H_4(NHC_6H_2Me_3)_2HgCl_2$, crystals melting at 150°. *Dinitrodipseudocumylethylenediamine*, $C_2H_4[NHC_6H(NO_2)Me_3]_2$, yellow powder, m. p. 97—98°; an *isomeride*, m. p. 49—50°. *Dipseudocumylpiperazine*, $Me_3H_2C_6N(C_2H_4)_2NC_6H_2Me_3$, colourless needles, m. p. 148—150°.

177. "The action of phenyl carbimide on diphenyl-, dialphyl-, and dinaphthyl-diamines." By Alfred Senier and William Goodwin.

When the two ethylenediamines described in the preceding abstract were treated with phenyl carbimide an interesting reaction resulting in the formation of ethylenediamines of the type $C_2H_4(NR'\cdot CO\cdot NHPh)_2$ was brought to light. These diamines are analogous to the ethylenediamine of Volhard (*Ann.*, 1861, **119**, 349), and to the trimethylene carbanilide of Hanssen (*Ber.*, 1887, **20**, 783). The reaction is shown to be a general one by the formation of the following homologues:—*Dicarbanilido-diphenyl-ethylenediamine*, $C_2H_4(NPh\cdot CO\cdot NHPh)_2$, m. p. 220°. *Dicarbanilido-ditolyl ethylenediamines*, $C_2H_4(NC_6H_4Me\cdot CO\cdot NHPh)_2$. The *ortho*-derivative

melts at 195—196°, the *meta*- at 181·5°, and the *para*- at 186°. *Dicarbanilido-dixylylethylenediamine*, $C_2H_4(NC_6H_3Me_2\cdot CO\cdot NHPh)_2$, melts at 167°. *Dicarbanilido-dipseudocumylethylenediamine*, $C_2H_4(NC_6H_2Me_3\cdot CO\cdot NHPh)_2$, m. p. 191°. *Monocarbanilidodi-α-naphthylethylenediamine*, $C_2H_4(NHC_{10}H_7)(NC_{10}H_7\cdot CO\cdot NHPh)$, m. p. 266°.

178. "Note on the action of nitrous acid on β-nitroso-α-naphthylamine." By Arthur Harden and J. Okell.

When β-nitroso-α-naphthylamine is treated in alcoholic solution with potassium nitrite and hydrochloric acid, it yields a potassium salt, $C_{10}H_6O_2N_3K$, which crystallises in reddish-coloured needles and decomposes vigorously at 250°. A different salt, described in a previous paper (*Ann.*, 1889, **255**, 148) was obtained by this reaction, which had the formula $C_{10}H_6O_4N_4KH$, and crystallised with $1\frac{1}{2}H_2O$, but on repeating the experiments the exact conditions necessary for the formation of this salt could not be ascertained, and the simpler salt, which differs from it by the elements of nitrous acid, was always obtained. Sodium nitrite yields the corresponding salt, $C_{10}H_6O_2N_3Na$. These salts behave towards acids in a manner similar to that already described, yielding, with hydrochloric acid and stannous chloride, a compound, $C_{10}H_6N_3\cdot OH$, which probably has the constitution of an imidazole, $C_{10}H_6<\overset{\quad N}{N(OH)}>N$ (compare Zincke and Schwarz, *Ann.*, 1900, **311**, 329). This substance crystallises with $1H_2O$, decomposes violently at 222°, and acts as an acid, yielding crystalline salts of sodium, potassium and barium. The silver salt has the formula $C_{10}H_6\cdot N_3OAg$, and not that previously ascribed to it. The acetate melts at 109°, and the silver salt yields colourless, crystalline derivatives when heated with methyl and ethyl iodides.

The isomeric α-nitroso-β-naphthylamine behaves towards nitrous acid in a similar manner, yielding a potassium salt, $C_{10}H_6N_3O_2K + H_2O$, which, with hydrochloric acid and stannous chloride, gives a compound, $C_{10}H_6N_3\cdot OH$, which decomposes at 245°, and is isomeric with that described above, which it closely resembles in its properties.

179. "1 : 2 : 4-Metaxylidine-6-sulphonic acid." By Henry E. Armstrong and L. P. Wilson.

One of the authors has on previous occasions discussed the conditions under which either ortho- or para- or meta-derivatives are formed from benzenoid amines, and has argued that meta-derivatives are pro-

duced by the direct attack of the benzene nucleus, whilst ortho- and para-compounds are formed by a process of isomeric change in which the radicle is transferred from the nitrogen into the nucleus. An opportunity of further testing this generalisation is afforded by 1 : 2 : 4-metaxylidine. When sulphonated by an excess of fuming acid, this is readily converted into the 5-sulphonic acid, the only metaxylidinesulphonic acid hitherto described; it was to be supposed that the 6-sulphonic acid would be readily obtained on heating the sulphate, and this proves to be the case.

When metaxylidine is mixed with a single molecular proportion of 100 per cent. sulphuric acid, and the mixture heated at 185° to 195° during 6 hours, the product then dissolved in water, and the solution neutralised with potassium carbonate, 90 per cent. of the theoretical amount of *potassium*-1 : 2 : 4 : 6-m-*xylidinesulphonate*, $C_6H_2(CH_3)_2(NH_2)\cdot SO_3K$, is obtained. *Potassium*-1 : 2 : 4 : 6-*aceto*-m-*xylidinesulphonate*, $C_6H_2NH(CH_3)_2Ac\cdot SO_3K$, is obtained by heating the potassium sulphonate with acetic anhydride. It is a colourless substance crystallising from alcohol in spindle-shaped needles. On adding bromine to its solution in water, the sulphonic group is not affected, although it is easily displaced from the unacetylated acid.

Potassium-1 : 3 : 5-m-*xylenesulphonate*, $C_6H_3(CH_3)_2\cdot SO_3K, \frac{1}{2}H_2O$, is obtained from the 1 : 2 : 4 : 6-*m*-xylidinesulphonate by diazotising, and then boiling with alcohol, or by means of the hydrazine; it crystallises from water in thin, colourless, lustrous leaves, and is nearly insoluble in alcohol. On fusing this salt with potash, it is converted into 1 : 3 : 5-*m*-xylenol, m. p. 65°. *Barium*-1 : 3 : 5-m-*xylenesulphonate*, $(C_6H_3Me_2\cdot SO_3)_2Ba, 2H_2O$, crystallises from water in fine, colourless leaves. 1 : 3 : 5-m-*Xylenesulphonic acid* crystallises from water in thin, transparent, flattened needles. 1 : 3 : 5-m-*Xylenesulphochloride*, $C_6H_3(CH_3)_2\cdot SO_2Cl$, crystallises from light petroleum and benzene in needles, and from chloroform in massive crystals; m. p. 94°. 1 : 3 : 5-m-*Xylenesulphobromide*, $C_6H_3(CH_3)_2\cdot SO_2Br$, resembles the sulphochloride in crystalline behaviour; m. p. 92—93°. 1 : 3 : 5-m-*Xylenesulphonamide*, $C_6H_3(CH_3)_2\cdot SO_2NH_2$, crystallises from water in very lustrous, colourless flakes, and from benzene in very fine needles; m. p. 134°. 1 : 3 : 5-m-*Xylenesulphanilide*, $C_6H_3(CH_3)_2\cdot SO_2\cdot NH\cdot C_6H_5$, crystallises from alcohol in large, monosymmetric crystals; m. p. 119°.

$$a : b : c = 0{\cdot}8718 : 1 : 0{\cdot}7341. \quad \beta = 110°58'.$$

1 : 3 : 5-m-*Xylenesulpho*-p-*toluidide*, $C_6H_3(CH_3)_2\cdot SO_2NH\cdot C_6H_4\cdot CH_3$, crystallises from alcohol in monosymmetric crystals resembling the anilide; m. p. 121—122°.

$$a : b : c = 1{\cdot}18195 : 1 : 0{\cdot}9380. \quad \beta = 101°7'.$$

180. "The preparation of acetylchloraminobenzene and related compounds." By F. D. Chattaway and K. J. P. Orton.

The authors reply to Armstrong's recent criticism of the authors' work. The statements which he calls in question are proved to be correct, and details are given of the method of preparing acetylchloraminobenzene. It is also shown that acetylchloramino-2 : 4-dichlorobenzene can be obtained by the direct action of chlorine on acetanilide.

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Idris, T. H. W. Notes on essential oils. Second edition. London 1900. From the Author.

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Rudorf, George. The periodic classification and the problem of chemical evolution. London 1900. From the Publishers.

II. *By Purchase.*

Glaser, Fritz. Indikatoren der acidimetrie und alkalimetrie. Wiesbaden 1901.

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At the next meeting, on Thursday, January 17th, 1901, the following papers will be communicated :—

"The preparation of esters from other esters of the same acid." By T. S. Patterson and Cyril Dickinson.

"Tecomin. A colouring matter derived from *Bignonia tecoma*." By T. H. Lee.

"A new method for the measurement of ionic velocities in aqueous solution." By B. D. Steele, B.Sc.